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**Frühdiagenetische Prozesse in jungen
Sedimenten von entstehenden Seen des
Braunkohletagebaus –
*am Beispiel der Flutung des Goitsche-
komplexes in Mitteldeutschland***

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Braunkohletagebaus**
am Beispiel der Flutung des Goitschekomplexes in Mitteldeutschland

Dissertation

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Inhaltsverzeichnis

	Seite
Danksagung	II
Inhaltsverzeichnis	IV
1 Einleitung	1
1.1 Gemeinsame Fragestellung der Manuskripte innerhalb des Gesamtprojektes	9
1.2 Kurzbeschreibung der Manuskripte	10
2 Eingereichte Manuskripte	13
2.1 Early diagenesis in sediments of a young acidic and a young neutral mining in Mid-Germany	15
2.2 Mesocosm studies for investigation of phosphorus retention in sediment during and after flooding of lignite mining lakes	58
2.3 Biogeochemical changes in acidic lignite lake after organic carbon and phosphorus supplementation	93
3 Zusammenfassung der Ergebnisse	126
3.1 Zusammenfassung der Einzelarbeiten	126
3.2 Zusammenfassung der Ergebnisse in Hinblick auf das Gesamtthema	131
4 Ausblick	135
5 Literatur	136
6 Datenanhang	140

1 Einleitung

Mit der Industrialisierung in Europa wurde auch in Deutschland der Abbau von Braunkohle auf Grund ihrer Nutzung als Brennstoff und als Ausgangsstoff für die chemische Industrie in zunehmenden Maß vorangetrieben. Mit der Gewinnung des Rohstoffs wurde es jedoch versäumt, die negativen Folgen auf die Umwelt mit in die Gesamtbetrachtung einzubeziehen. In der Folge des Tagebaus entstanden flächenmäßig sehr große Areale, die rekultiviert wurden oder werden sollen. In Deutschland existieren 6 Braunkohlereviere, wovon zwei in den neuen Bundesländern liegen - das Lausitzer Revier und das Mitteldeutsche Revier. Als Ergebnis eines lang anhaltenden Braunkohletagebaus verblieb eine Landschaft aus "natürlichen Restzellen" (Reste einstiger Auenlandschaften, Waldgebiete, Flurgehölze), große Betriebsflächen (offene Tagebaue, Restlöcher, Kippenflächen, Halden), durch Wiedernutzbarmachung und Sukzession gestalteten Folgelandschaften (Kippenäcker, Tagebaurestseen, trockene Hohlformen, Vorrangflächen für Naturschutz) sowie Hinterlassenschaften von Industrie und Entsorgung (Industriebrachen, Altablagerungen, Deponien) (Berkner 1998). Die Mehrzahl der Tagebaue wurde infolge des drastischen Rückgangs des Bedarfs an Braunkohle im östlichen Teil Deutschlands nach 1990 mitten im Betrieb stillgelegt, was zu zusätzlichen negativen Folgen für die Umwelt führte. Zum einen waren die Böschungen nicht sachgerecht befestigt, zum anderen stellte die notwendige schnelle Füllung der Restlöcher mit Wasser aus wasserhaushaltlicher Sicht ein erhebliches Problem dar.

Während des Abbaus der Kohle mußte der Grundwasserspiegel in den betroffenen Gebieten weiträumig gesenkt werden, was mit beträchtlichen Einfluß für den Gebietswasserhaushalt verbunden war. Es führte zu tagebauübergreifenden Absenkungstrichtern und zu großräumigen Veränderungen der Grundwasserströme.

Infolge der "Trockenlegung" der Gebiete und der Bergbauaktivitäten wurde dem anoxischen Untergrund und den aufgeschütteten Abraumhalden der Zutritt von Luftsauerstoff gewährt, so dass eine anthropogen initiierte Oxidation stattfand. Häufig ist die Kohle mit reduzierten Eisen- und Schwefelverbindungen vergesellschaftet (Evangelou 1995). Im besonderen handelt es sich um Pyrit und andere Sulfidminerale, die bei einer Oxidation zur Bildung von Fe^{2+} , SO_4^{2-} und H^+ führen. Aber auch die Freisetzung von hohen Konzentrationen an Aluminium und Schwermetallen konnte in diesem Zusammenhang beobachtet werden. Diese Oxidationsprodukte sammelten sich in den Abraumkippen an und werden infolge des Anstiegs des Grundwassers durch die Stilllegung der Tagebaue als Restseewasser in die Restlöcher eingespült. Sofern im durchströmten Untergrund und in den Kippen keine oder nur ungenügend abpuffernde Substanzen wie Carbonate, Silikate und Eisen- und Manganoxide vorhanden sind, führt dieser Prozess zur Entstehung von sauren Restseen. Die Oxidationsprozesse können in drei Schritte unterschieden werden (Gl.1-3), die sich neben verschiedenen hohen Konzentrationen an Reaktionsprodukten durch unterschiedliche Reaktionsgeschwindigkeiten auszeichnen. Pyrit wird mit Luftsauerstoff und durch dreiwertiges Eisen oxidiert. Letzteres entsteht bei der Oxidation von Fe^{2+} durch Luftsauerstoff. Durch chemoautotrophe Bakterien und acidophile Schwefeloxidierer wird die Reaktionsgeschwindigkeit bei pH Werten unter 4 um das drei- bis zehnfache erhöht (Nordstrom 1985).

Auch die Hydrolyse von Fe^{2+} , die sich beim Eintritt in den Restsee vollzieht, hat eine weitere Versauerung des Wassers zur Folge (Gl. 4)





In Abhängigkeit vom pH-Wert der Seen konnten unterschiedliche Eisenhydroxide festgestellt werden. Während in neutralen Restseen überwiegend Goethit und Ferrihydrit vorkommen, wird bei sauren Verhältnissen besonders Schwertmannit gebildet (Peine 1998, Peine et al. 2000). Vergleichbare saure Wässer, die jedoch nicht unbedingt in Form von Seen vorkommen, sind als Acid Mine Drainage (AMD) vor allem aus Amerika bekannt (Bigham et al., 1990, Schwertmann et al., 1995). Diese Wässer haben als Produkte von Bergbautätigkeiten ähnliche chemische Zusammensetzungen wie die der Restseen. Die Eisen- und Sulfatkonzentrationen liegen bei sauren Restseen (pH 2-3) in Deutschland im allgemeinen zwischen 10 mmol/l und 25 mmol/l (Friese et al. 1998, Peine 1998, Geller and Schultze 1999, Stottmeister et al. 1999, Frömmichen 2001).

Je nach dem Puffervermögen des Seewassers und der Zusammensetzung vom Sicker- und Grundwasser werden verschiedene pH Werte als Maß der unterschiedlichen Versauerungszustände erreicht. Für die Fe^{3+} gepufferten Systeme liegt der pH-Wert bei 3, für Al^{3+} gepufferte Systeme bei 5 und für carbonat gepufferte Systeme im neutralen Bereich (Stottmeister et al. 1999).

Die Besiedlung von sauren Restseen (pH 2-3) mit höheren Lebewesen ist sehr eingeschränkt. Das Ökosystem wird vor allem besiedelt von wenigen säuretoleranten und speziell angepassten Mikroorganismen (Deneke 2000, Deneke and Nixdorf 1997), säuretoleranten Wasserinsekten (Wollmann 1997a, b) und einigen weniger säureempfindlichen höheren Wasserpflanzen (Pietzsch

1979). Andere höhere Organismen wie Fische, Krebstiere und Mollusken kommen in den sauren Gewässern nicht vor. Die Ursachen einer geringen Primärproduktion dieser Seen werden in dem pH bedingten geringen Angebot an gelöstem CO₂ und geringen Nährstoffkonzentrationen wie Phosphor gesehen, die für Algen als limitierende Faktoren wirken können (Gyure et al. 1987, Deneke and Nixdorf 1997, Kapfer et al. 1997, Kapfer 1998). Allerdings ist die Bioaktivität vergleichbar mit neutralen Seen.

Geht man von den gesetzlichen Grundlagen zum Schutz und der Nutzung von Gewässern aus, so können diese Seen weder für die Fischerei, Trinkwassergewinnung, zur Bewässerung landwirtschaftlicher Flächen noch als Badegewässer genutzt werden (Geller und Schultze 1999). Weiterhin wirken die sauren Wässer als Gefahrenquelle für angrenzende Wasserkörper, die bei ungünstigen hydrologischen Verhältnissen durch den Abstrom kontaminiert werden können. Somit liegt es im öffentlichen Interesse, die Entstehung dieser schwefelsauren Seen zu verhindern oder geeignete Sanierungen an den bereits bestehenden Seen vorzunehmen.

Es gibt vergleichbar stark schwefelsaure natürlich entstandene Vulkanseen in Japan, Kamschatka, Indonesien, Süd- Mittel- und Nordamerika, an die diese Bewertungskriterien nicht anzulegen sind, sie werden als Naturdenkmale eingestuft (Ergorov et al. 1998, Geller and Schultze 1999). Insofern sind die Bewertungsmaßstäbe an die Gewässer immer von den Zielvorgaben abhängig. Nach LENAB (1997) sollte zur Diskussion stehen, ob saure Bergbaurestseen im jedem Fall als Sanierungsobjekte einzustufen sind oder auch als Extrembiotop erhaltenwert sein können.

Zur Sanierung der entstehenden und entstandenen Gewässer haben sich vom derzeitigen Stand der Wissenschaft und Technik mehrere Strategien herauskristallisiert, die u. a. bei Schultze et al. (1999) zusammengestellt sind. Der beste Weg wäre eine Prävention, die eine Hemmung der Pyritoxidation zum Ziel hätte. Dies ist z. B. durch kurze Expositionszeiten pyrithaltiger

Materialien, einen schnellen Grundwasseranstieg, Zufuhr sauerstoffzehrender Stoffe und/oder der Anreicherung der Kippen mit Alkalität liefernden Stoffen wie Kalk möglich. In den wenigsten Fällen wurden diese Maßnahmen zu Beginn des Abbaus der Kohle mit in Betracht gezogen.

Wenn ein Restsee bereits mit Grundwasser gefüllt ist und saure pH Verhältnisse vorliegen, gibt es die Möglichkeit der Restauration, die Maßnahmen zur Sanierung im See selbst beinhalten und zu einer Neutralisation des Gewässers führen. Die Alkalisierung des aciditätsbeladenen Wassers auf dem Weg zum See würden durch Maßnahmen zur nachträglichen Einbringung von Kalk oder Asche in die Kippen gefördert werden, um das zuströmende Sickerwasser mit Alkalität anzureichern. Die Verdünnung und Verdrängung des sauren Wassers durch die Einleitung von neutralen oberirdischen Gewässern und die Ausbringung von Neutralisationsmitteln führt zur Neutralisation auf chemischen Wege.

Peine (1998) stellt Möglichkeiten der Neutralisierung innerhalb einer Bergbauseenkette dar, die auf einer gezielter Ausfällung von Eisen beruhen, indem der erste durchströmte See als "Vorklärbecken" fungiert und einen großen Teil der Säure abfängt. Die organische Substanz, die als limitierender Faktor bei der Sulfidbildung gilt, steht in den anschließenden Seen für die Prozesse der Sulfatreduktion zur Verfügung. Weiterhin kann eine Neutralisation durch Alkalität produzierende biologische Prozesse im See selbst erzeugt werden. Dabei werden über eine gezielte Eutrophierung oder über die Einbringung mikrobiell verwertbarer organischer Stoffe (Davison et al. 1989, George and Davison 1998, Fyson 1998, Frömmichen 2001) frühdiagenetische Prozesse wie die Sulfat- und Eisenreduktion, verbunden mit einer Festlegung von Eisensulfiden initiiert, die eine zunehmende Neutralisierung zur Folge haben (Klapper et al. 1996, Schultze et al. 1999, Frömmichen 2001). Der Erfolg dieser Methode ist jedoch bisher im Vergleich zu herkömmlichen Maßnahmen noch nicht an bestehenden Seen belegbar. Da aber

bereits viele Bergbauseen im Zustand extrem saurer Verhältnisse existieren, ist nach Schultze et al. (1999) eine wachsende Bedeutung dieser Verfahren zu erwarten.

Ein weiterer Ansatz verhindert den Säureeintrag aus den Kippen und dem Untergrund durch eine schnelle Fremdflutung der Restlöcher mit Wasser aus Flüssen oder aktiven Tagebauen. Hierbei wird ein vom See weg gerichtetes Gefälle der Grundwasseroberfläche erzeugt, so dass Kippenwässer nicht in den See gelangen können. Zusätzlich bewirkt eine schnelle Flutung mit Flußwasser im Gegensatz zu einer wesentlich langsameren Flutung mit Grundwasser, dass der Kontakt bzw. das Eindringen von Luftsauerstoff in pyrithaltige Sedimentschichten durch die Wasserbedeckung unterbrochen wird. Der Prozess der Oxidation kann somit sehr viel schneller gestoppt und die weitere Säurebildung verhindert werden. Bei dieser Variante gibt es auch die Mischform zwischen der Füllung mit Grund- und Oberflächenwasser, die infolge von auftretenden Wechselwirkungen für die Steuerung der Wassergüte genutzt werden kann (Klapper 1995). Die Flutung kann als einmalige Befüllung des Restlochs vollzogen werden oder in Form eines Durchflusses erhalten bleiben, so wie es bereits beim Muldestausee oder beim Tagebausee Golpa Nord (Mitteldeutschland) realisiert worden ist. Der Vorteil der Durchflußmaßnahme besteht in der ständigen Verdünnung des bereits vorhandenen sauren Restseewassers und der darin enthaltenen hohen Konzentrationen an toxisch wirkenden Stoffen. Zusätzlich werden in durchflossenen Bergbauseen Stoffe zurückgehalten, wobei die Eliminierungsleistungen für die Wasserinhaltsstoffe unterschiedlich hoch sind (Klapper 1995). Im Fall des Muldestausees sedimentiert ein großer Teil der Schwebstoffe im See infolge verringerter Fließgeschwindigkeit.

Die einmalig Füllung der Restlöcher mit Flußwasser hat den Vorteil, dass der See nicht die Funktion als ständige Senke übernimmt. Ein wesentliches Problem bei der Fremdflutung durch Flußwasser stellt die Wasserbeschaffenheit des Flutungswassers dar, da sie die Wassergüte des

entstehenden Sees grundlegend beeinflusst. In dicht besiedelten Räumen weisen Flußwässer häufig hohe Konzentrationen an Nährstoffen auf, die bei Seen zur Eutrophierung führen können. Besonders die Phosphorkonzentrationen nehmen dabei eine Schlüsselrolle ein. Durch das Absinken von organischen und anorganischen Partikeln kann Phosphor im Sediment angereichert werden. Dem seeinternen Kreislauf wird er jedoch nicht entzogen, da Phosphor durch frühdiagenetische Prozesse im Sediment freigesetzt und über Diffusion in das Bodenwasser transportiert werden kann. Zu den wichtigsten Prozessen gehören dabei die Remineralisierung von organischer Substanz und die Auflösung von Eisenhydroxiden. Da die Bergbaurestseesedimente zum großen Teil mit Eisen angereichert sind, nimmt der Eisenkreislauf eine besondere Bedeutung ein.

Der mikrobielle Abbau des organischen Materials findet unter Reduktion verschiedener Oxidationsmittel statt. Nach der klassischen Modellvorstellung von Fröhlich et al. (1979) richtet sich die Abfolge der terminalen Elektronenakzeptoren nach dem größt möglichen Energiegewinn für die Mikroorganismen: O_2 , NO_3^- , $Mn(IV)$, $Fe(III)$, SO_4^{2-} , CO_2 . Unter der Annahme einer vollständigen Umsetzung entstehen als Produkte der Reaktionen die jeweiligen reduzierten Spezies und CO_2 sowie H_2O . Viele Untersuchungen zeigen jedoch, dass es nicht immer zum vollständigen Abbau der organischen Substanz kommen muß, sondern die Umsetzungsprozesse mit der Entstehung von anderen organischen Produkten enden (z.B. Lovley and Klug 1986, Lovley and Phillips 1989, Lovley 1991).

Es ergibt sich eine Tiefenzonierung für wassergesättigte Sedimente, die unterschiedliche Redoxzustände repräsentieren. Andere Arbeiten weisen nach, dass keine strikte Trennung dieser Reaktionsbereiche existieren muß (Sørensen 1982, Canfield 1993). Nach Wallmann (1990) können die Eisen- und Sulfatreaktion auch parallel ablaufen. Mehrfach konnten in Seesedimenten

auch horizontale Zonierungen mit zunehmender Tiefe der Seen nachgewiesen werden. Dies beruht auf den unterschiedlichen Geschwindigkeiten von Transport - und Reaktionsprozessen. Die Umsetzungsraten sind dann im Vergleich zu den Transportraten höher .

Die Bedeutung der einzelnen Reaktionen zum Abbau der organischen Substanz ist je nach System unterschiedlich und wird von den mikrobiellen und geochemischen Bedingungen bestimmt. Die gesamte Abbaurate ist von der Menge des eingetragenen organischen Kohlenstoffs abhängig, der mikrobiell gut verfügbar ist. Je höher die Abbaurate desto mehr reduzierte Spezies können ins Porenwasser freigesetzt und durch molekulare Diffusion entsprechend dem Konzentrationsgradienten transportiert werden. Da diese Reaktionen besonders in oberflächennahen Sedimentschichten stattfinden, wird häufig ein ins Freiwasser gerichteter Flux des Spezies festgestellt, der zu erhöhten Konzentrationen im Bodenwasser führt. Aber auch der ins Sediment gerichtete Transport der gelösten Spezies wurde in vielen Arbeiten festgestellt. Gelangen die Spezies in andere geochemische Verhältnisse, so kann es zur Ausfällung entsprechender Mineralphasen kommen. Für die einzelnen Diagenesebereiche gibt es charakteristische authigene Mineralbildungen wie z. B. Fe(III)- und Mn(IV)-Oxide und Hydroxide, Vivianit, Siderit, Pyrit und andere Fe-Sulfide.

Bei der vorliegenden Arbeit wird die Fe-Diagenese in den Vordergrund der Untersuchungen gestellt, die durch biotische und/oder abiotische Reaktionen gesteuert werden kann. Liegen Eisenhydroxide in gut verfügbarer Form für Fe(III)reduzierende Bakterien vor, können sie durch mikrobielle Reduktion gelöst werden. Durch die Gegenwart von Reduktionsmitteln wie S^{2-} und CH_4 , die Produkte von frühdiagenetischen Prozessen sind, kann es zur abiotischen Reduktion von Fe(III) kommen. Weiterhin kann die Änderung der Milieubedingungen zur Instabilität von Eisenhydroxiden und deren Auflösung führen. Die Neubildung von Fe-Mineralphasen findet in

Abhängigkeit von den geochemischen Bedingungen in Form reduzierter Spezies Fe(II) wie z. B. Siderit /Pyrit oder in oxidierter Form Fe(III) wie z. B. Goethit statt. Die einzelnen Reaktionen der Redoxreaktionen verlaufen rein thermodynamisch und/oder unter mikrobieller Hilfe.

1.1 Gemeinsame Fragestellung der Manuskripte innerhalb des Gesamtprojektes

Ziel des Forschungsvorhabens zur Flutung des Tagebaus Goitsche war es, eine Prognose für die Entwicklung der Wasserbeschaffenheit der zukünftigen Seen abzugeben. Hierbei war die physiko-chemische und biologische Beschaffenheit bereits bestehender Restseen zu erfassen und die vorgesehene Fremdfutung des Tagebaus mit Flußwasser der nahegelegenen Mulde zu beurteilen. Es sollte das mögliche Eutrophierungspotential des zukünftigen Seensystems abgeschätzt werden. Dieses ist neben der Einbringung von Nährstoffen durch das Muldewasser im besonderen abhängig von biogeochemischen Prozessen in den relativ jungen Sedimenten der Tagebauseen während und nach der Flutung. Die Beurteilung dieser möglichen Eutrophierungspotentiale ist Zielstellung der vorliegenden Arbeit. Die Manuskripte befassen sich sowohl mit den noch wenig untersuchten frühdiagenetischen Prozessen in Bergbaurestseesedimenten, die sich innerhalb von 6-8 Jahren gebildet haben, als auch mit der zu erwartenden Dynamik der Prozesse, die im Zuge der Flutung im Zusammenhang mit der Festlegung und Remobilisierung von Phosphor eine wesentliche Rolle einnehmen. Weiterhin war es ein Ziel, diese Prozesse in Hinsicht auf die Ableitung der Stoff-Flüsse von Phosphor quantitativ zu beurteilen, um die Gewässergüteentwicklung besser abzuschätzen. Die

Untersuchungen wurden an Sediment-, Poren- und Bodenwasserproben des sauren Restsees Niemegk und des neutralen Restsees Döbern durchgeführt. Für Sediment-Wasser Inkubationsversuche im Labor wurden ungestörte Sedimentkerne aus dem Restsee Niemegk entnommen.

Von dem Fallbeispiel des Tagebaus Goitsche ausgehend ist es geplant, die gesamten Ergebnisse der Untersuchungen auf Flutungsszenarien anderer Gebiete unter Berücksichtigung der jeweiligen Standortfaktoren zu übertragen.

1.2 Kurzbeschreibung der Manuskripte

Im folgenden Abschnitt werden die eingereichten Manuskripte, die im nächsten Kapitel in vollständiger Form enthalten sind, inhaltlich kurz erläutert. Das erste Manuskript (Kap. 2.1) befaßt sich mit grundlegenden frühdiagenetischen Prozessen in oberflächennahen Sedimenten von zwei bestehenden Tagebaurestseen der Goitsche, die die Geochemie in den Sedimenten wesentlich beeinflussen und den Ausgangszustand der zu flutenden Restseesedimente repräsentieren. In den beiden nächsten Manuskripten (Kap. 2.2 und 2.3) werden zu erwartende wichtige biogeochemische Veränderungen in den Sedimenten an Hand von Laborexperimenten erfaßt, die sich im Zuge der Flutung der Tagebaurestseen mit Flußwasser ergeben.

Während zwei Manuskripte selbständig verfaßt worden sind, beschränkt sich der Beitrag im dritten Manuskript auf die Verfassung der Abschnitte der geochemischen Ergebnisse und Diskussion. Die Arbeiten der Co-Autoren zu den einzelnen Manuskripten werden in den Beschreibungen im einzelnen dargestellt.

C. Langner, C. Hensen , S. Kellner and K. Wendt-Potthoff: Early diagenesis in sediments of a young acidic and a young neutral mining lake in Mid-Germany.

Die Ergebnisse des Manuskriptes basieren auf geochemischen und mikrobiologischen Untersuchungen, die überwiegend an Porenwässern und Sedimenten von zwei Bergbaurestseen mit unterschiedlichen Milieuverhältnissen (Tagebaukomplexes Goitsche) durchgeführt wurden. Im Vordergrund stand dabei die Erfassung des Ausgangszustandes der Sedimente hinsichtlich der wesentlichen biogeochemischen Prozesse, welche einen starken Einfluß auf geochemische Verhältnisse in den Sedimenten und auf das überströmende Wasser haben. Durch die Ergebnisse einer geochemische Modellierung können die Aussagen zu den aufgezeigten Prozessen unterstützt werden.

Diese Modellierung wurde in Zusammenarbeit mit mir von C. Hensen durchgeführt, der damit einen wichtigen Beitrag für die Auswertung der Arbeit lieferte. Durch die von K. Wendt-Potthoff eingebrachten Ergebnisse zur Aktivität der Eisenreduktion als auch zahlreiche Diskussionsanregungen zu mikrobiologischen Themen konnte die Bewertung der ablaufenden Prozesse umfassender gestaltet werden. S. Kellner unterstützte mich bei den geochemischen Berechnungen mit PHREEQC (Parkhurst 1995).

C. Langner and K. Friese : Mesocosm studies for investigation of phosphorus retention in sediment during and after the flooding of lignite mining lakes.

In diesem Artikel werden Ergebnisse von Inkubationsexperimenten an Sediment-Wasser-Systemen ausgewertet, die dazu dienen, geochemische Verhältnisse während und nach der Flutung der Tagebaurestseen mit Flußwasser zu simulieren. Ziel ist es, wichtige frühdiagenetische Prozesse zu charakterisieren, die zu Veränderungen im Sediment führen und Einfluß auf die Zusammensetzung des überströmenden Wasser haben. Besonderen Schwerpunkt bilden dabei Umsetzungsprozesse, die die Phosphormobilität beeinflussen und zu Konzentrationsänderungen von Phosphor im überströmenden Wasser beitragen können. Es wird eine Einschätzung gegeben unter welchen Milieubedingungen wieviel Phosphor remobilisiert, festgelegt oder ins Seewasser freigesetzt werden kann.

Durch eine Übertragung der Ergebnisse auf Seeverhältnisse wird abgeschätzt, in welchem Maße die Sedimente als Quelle oder Senke für eingetragenen Phosphor fungieren und wie eine mögliche Eutrophierung durch die Flutung mit Flußwasser hinsichtlich dieser Prozesse einzuschätzen ist.

K. Friese unterstützte die Arbeit sowohl durch Anregungen zum Entwurf und zur Durchführung der Laborexperimente als auch inhaltlich durch zahlreiche Diskussionen.

K. Wendt-Potthoff and C. Langner: Biogeochemical changes in acidic lignite mining lake sediment after organic carbon and phosphorus supplementation.

Schwerpunkt dieses Manuskriptes bildet die Erfassung von mikrobiologischen und geochemischen Veränderungen in den Sedimenten, die durch die Zugabe von organischem Kohlenstoff und Phosphor initiiert werden und mit Hilfe der Auswertung von oben genannten

Laborexperimenten erfaßt wurden. Die Abhängigkeit dieser Prozesse von unterschiedlichen Milieubedingungen im überströmenden Wasser ist ebenfalls berücksichtigt und ausgewertet worden. Mittelpunkt der Untersuchungen bilden Prozesse, die mit dem Eisen- und Schwefelkreislauf in den Sedimenten im engen Zusammenhang stehen. Es werden signifikante Merkmale aus geochemischer und mikrobiologischer Sicht herausgearbeitet und stationäre sowie instationäre Zustände in den Sedimenten aufgezeigt.

Die mikrobiologischen Arbeiten wurden vollständig von K. Wendt-Potthoff durchgeführt. Bis auf die geochemischen Abschnitte wurde das Manuskript von ihr verfasst.

2 Eingereichte Manuskripte

Dieses Kapitel enthält die drei vollständigen Manuskripte, die jeweils um die Danksagungen gekürzt wurden.

Die Planung der Geländeuntersuchungen und die Entwicklung des Designs zur Durchführung der Inkubationsexperimente, deren Installation und Betreuung wurde vollständig von mir durchgeführt. Die Probenahmen im Gelände und im Rahmen der Inkubationsversuche, die Porenwasser- Extraktions- und zum Teil die Festphasenuntersuchungen wurden von mir in Zusammenarbeit von Technikern und Mitarbeitern der Analytik der Sektion Gewässerforschung durchgeführt. Die Bestimmung der Festphase auf die Elementzusammensetzung (RFA) erfolgte von Herrn Dr. Morgenstern vom UFZ (Sektion Analytik). Die Untersuchungen zur mineralogischen Zusammensetzung (RDX, Mößbauer Spektroskopie) sind von Herrn Gruner (Universität Freiberg) und von Frau Dr. McCammon (Bayrisches Geoinstituts der Universität Bayreuth) durchgeführt worden. Die geochemischen Berechnungen mit PHREEQC im zweiten

Manuskript sowie die Auswertungen aller Untersuchungs- und Modellierungsergebnisse in den eingereichten Manuskripten wurden mit Ausnahmen der mikrobiologischen Arbeiten (Manuskript 3) von mir vorgenommen.

2.1

Early diagenesis in sediments of a young acidic and a young neutral mining lake in Mid-GermanyC. LANGNER¹, C. HENSEN², S. KELLNER¹ AND K. WENDT-POTTHOFF¹¹ UFZ - Centre for Environmental Research, Department of Inland Water Research, Brückstrasse 3a, 39114 Magdeburg, Germany² University of Bremen, Department of Geosciences, P.O. Box 330440, Germany

Abstract —In order to forecast the development of water quality of lakes resulting from opencast mining it is necessary to understand the interactions between lake sediments and the water body. Therefore sediments of an acidic and a neutral mining lake were investigated in a closed lignite mine in Mid-Germany (Goitsche near Leipzig). The small water bodies were formed by ascending groundwater within the last six years. Sediment cores of each lake were taken four times in 1997/98. Physicochemical parameters (O_2 , pH, E_H) were determined and the pore waters were investigated for Fe, Mn, DOC, SO_4^{2-} , nutrients and heavy metals (Zn, Ni, As). The geochemical and mineralogical composition of solid phases were determined once for each lake. Fe(III) reduction potentials were determined for acid sediments in May 1998. The main composition of solid phases were similar for both sediment types, whereas the pore water profiles exhibited significant differences. In the acid mining lake sediments the distribution of pH, E_H , Fe, SO_4^{2-} and DOC in pore waters showed temporal changes. In the neutral mining lake sediments the geochemical conditions were more constant. In both sediment types Fe-oxidation and -precipitation at the sediment surface and the dissolution of Fe-hydroxides in upper layers are dominant biogeochemical processes. In the sediment of the acidic lake the pH-value is mainly controlled by the transformation of schwertmannite to goethite, especially in the upper 10 cm, and

microbial reduction of Fe(III) is connected to decomposition of organic matter in discrete zones. The combined processes -as postulated- were implemented to a non steady state numerical model and their validity was verified by pH modeling. Geochemical modeling indicated that the ratio of rates of schwertmannite transformation and Fe(III) reduction controls pH values in the sediments and makes them a geochemically instable system. In contrast to the acid mining lake sediments the neutral lake sediments a higher proportion (10%) of Fe(II) was bonded as carbonate, in form of siderite. Furthermore our study indicated the formation of H₂S and its precipitation as FeS and FeS₂ in low concentrations in the neutral lake sediment.

INTRODUCTION

In Mid-Germany lignite has been mined in large opencast operations for decades. During mining the groundwater table was artificially lowered in wide areas. Sulfidic minerals in previously unsaturated sediment zones were oxidized due to contact with oxygen, which lead to the release of Fe, SO₄²⁻ and H⁺. After termination of mining the groundwater table raised again, and small lakes developed which are enriched with dissolved substances from the sediment zones flown through by groundwater (Fe, SO₄²⁻, Al, heavy metals and acidity). In order to stop oxidation in unsaturated zones, raise the pH-values and prevent further inflow of acidity, flooding of the mine pit with river water is the method of choice in many cases (Schultze et al., 1999 and references therein). However, the high nutrient load of the river water may lead to eutrophication of the system (Klapper and Schultze, 1995). In order to predict and manage water quality of the developing lakes, investigation of already existing mining lakes is necessary. The lake sediments play a key role in determination of water quality during early diagenetic processes, especially the

interrelated biogeochemical cycles of C, Fe, S, and P (Friese et al., 1998; Hupfer et al., 1998; Peiffer and Peine, 1998). Iron transported into the lake is oxidized and precipitated as Fe oxyhydroxides. This reaction releases protons, so Fe^{2+} can be regarded as a source of acidity. Precipitating Fe(III)oxyhydroxide can adsorb large quantities of SO_4^{2-} , PO_4^{3-} , heavy metals and organic substances which are therefore enriched in the lake sediments. Early diagenetic processes in those sediments are determined by the mainly biologically controlled transformation of iron minerals, by microbial sulfate reduction and sulfide oxidation (Graff and Nèveke, 1985; Mills et al., 1989; Blodau et al., 1998). During degradation of bioavailable organic material, reductive processes can lead to release and transfer of the above mentioned substances. Availability and degradation of organic material is believed to be the key for the activity of microorganisms and therefore controls the intensity of the reactions. To improve our understanding of these processes, the sediments of a neutral and acidic young mining lake in the same mine were investigated with geochemical and microbiological methods and discussed using the results of geochemical modeling.

MATERIALS AND METHODS

Study Area

The two investigated lakes were formed approximately 6 years before the study period in a closed lignite mine in Mid-Germany (Fig.1). Since then a sediment layer of 20 to 40 cm has been deposited, which we investigated geochemically. Table 1 gives essential geochemical and physical characteristics of the lakes. Lake Niemegek is extremely acidic ($\text{pH} < 3$). Its chemical composition is strongly influenced by the products of pyrite oxidation in silty sediments ('Bernsteinschluff', silt rich in amber) in the underground. The second artificial Lake Doebern has

a neutral pH value. Both lakes are characterized by high concentrations of iron and sulfate, however the acidic Lake Niemegek is extremely high in both. The DOC (dissolved organic carbon) and nutrient concentrations of Lake Niemegek are very high compared with other mining lakes (Herzprung et al., 1998) due to permanent inflow of groundwater. Especially the phosphorus concentration is four times higher in the inflow than in the lakes. This indicates a P-elimination in the mining lakes caused by sedimentation processes. The lakes are strongly influenced by groundwater and dissolved substances from the layers flown through. During the study period the lakes were not typically stratified (Boehrer et al., 2000), in summer we observed anoxic conditions near the sediment surface.

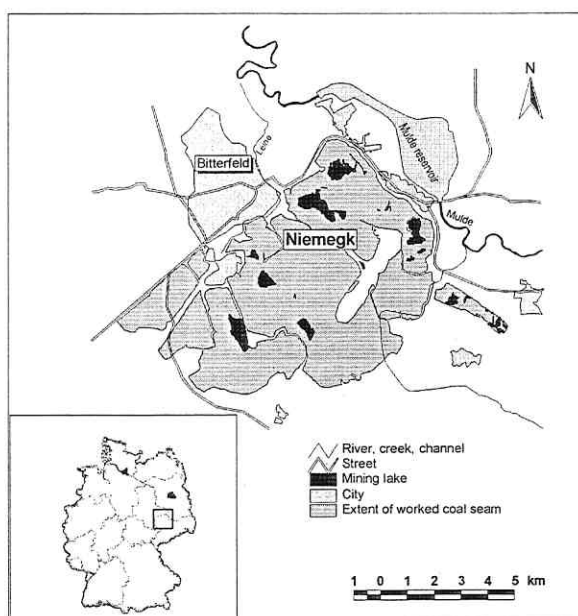


Fig.1: Map of study area.

Tab. 1: Geochemical and physical characteristics of Lake Niemegek and Lake Doebern (Limnological Expertise, 1997)

	Lake Niemegek	Lake Doebern (subbasin)
Surface area (10^6 m^2)	0.7	0.34
Volume (10^3 m^3)	7.7	1.2
Maximum depth (m)	15	14
pH	2.6 - 3.1	6.4 - 7.1
sulfate (mg/l)	2000	720-1210
iron (mg/l)	230	0.4-9
soluble reactive phosphorus ($\mu\text{g/l}$)	30-90	1-5
dissolved organic carbon (mg/l)	4-9	2.9-3.5
mean water residence (years)	356	54

Sample Collection and Pore Water

In April, July and October of 1997 and May 1998 sediment cores were obtained from both lakes at defined locations marked by buoys. Sediment was collected in 9 cm diameter polycarbonate tubes with a gravity corer (Uwitec, Mondsee, Austria) which yielded apparently undisturbed cores. Immediately after collection the O_2 concentration profiles in the cores were measured with a microelectrode (MASCOT). Then cores were transferred into a glove box filled with nitrogen. They were sectioned in slides of 1 cm (0-10 cm depth) or 2 cm (10-20 cm depth) and transferred into 50 ml polyethylene centrifuge tubes. From 20 cm to the bottom sectioning proceeded cm-wise, but only every 2nd or 3rd slice was analyzed. Samples were homogenized, and pH and E_H values were measured with electrodes (SENTIX-41, SENTIX-ORP, WTW). Subsamples for extraction of iron bonded forms and for Fe(III)reduction potential were filled into centrifuge tubes and into sterile brown glass vials. In addition we filled 2 ml microtubes for determination of water content and porosity. Tubes for pore water collection were centrifuged at 3800 rpm for 10 minutes and returned to a glove bag where pore water was collected into plastic syringes and

filtered through 0.45 μm cellulose acetate filters. Before use the filters were washed with 60°C hot distilled water in order to minimize background DOC concentrations. Samples were diluted with HCl-acid water (pH 2) for determination of SRP (soluble reactive phosphorus), NO_3^- , NH_4^+ , SO_4^{2-} , DOC and Fe^{2+} . Nutrients were immediately measured photometrically with a Segmented-Flow-Analyzer (SANPLUS, SKALAR). Fe^{2+} was determined with a spectrophotometer (DU-600, BECKMAN) using Ferrozine according to Stookey (1970). DOC concentrations were obtained using a carbon-analyzer (DIMATOC-100, DIMATEC). SO_4^{2-} was analyzed with a ion-chromatograph (ICA-5000, GAT). Remaining pore water was acidified with HNO_3 and stored at 4°C in brown glass vials until further analysis. Main elements and heavy metals in the pore waters were determined with ICP-OES (OPTIMA-6000, PERKIN-ELMER) and ICP-MS (ELAN-5000, SCIEX and PERKIN-ELMER).

Solid Phases

After extraction of pore water the remaining solids were frozen at -40°C and later freeze-dried. To remove residual humidity, the material was subsequently dried at 50°C for 24 h. Dry samples were treated with a mortar and pestle and homogenized. This material (<63 μm) was used for RFA analysis of elemental composition (SRS-3000, SIEMENS). Total and organic C, S and N were determined with the element analyzer (VARIO EL, ELEMENTAR). Anorganic carbon content was determined as the difference between total and organic carbon. Mineralogy was investigated by RDX. In May and November 1998 sediment traps were exposed at the marked sampling points for 2 weeks. Trapped material was treated and analyzed like sediment material from the cores.

Extractions

Extractions were only performed with selected cores. In July 1997 and May 1998, sediments were extracted for Fe(III)oxide fractions. Acid Volatile Sulfide (AVS) and Chromium Reducible Sulfide (CRS) were also determined in four selected sediment samples in October 1997.

Subsamples were weighed before extractions. For the extraction of poorly crystalline and crystalline Fe(III)oxides the scheme of Haese (1997) (modified from Kostka and Luther, 1994; Ferdelmann, 1988; Lord, 1980) was used. Wet sediment material (approximately 1 ml) was sequentially extracted 24 h with 30 ml of ascorbate and 1 h with 20 ml of dithionite solutions. Fe concentrations in filtered extracts were measured by ICP-OES. Acid Volatile Sulfide (AVS: $\text{H}_2\text{S} + \text{FeS}$) and Chromium Reducible Sulfide (CRS: FeS_2) were extracted from wet sediment subsamples. The distillation procedure was adapted from Haese et al. (1997), Fossing and Jørgensen (1989) and Canfield et al. (1986). Samples were distilled at room temperature in order to avoid extraction of S° . H_2S was swept by carrier gas into a trap with SAOB (Sulfur Antioxidant Buffer) solution (Cornwell and Morse, 1987). Sulfide concentrations were determined by polarography (MDE-150, RADIOMETER, Inc).

HCl-soluble Fe(II) and hydroxylamine-reducible Fe(III) were determined in triplicates according to Lovley and Phillips (1987). Samples were centrifuged (14.000 rpm, 10 min) instead of filtration before photometry.

Fe(III) Reduction Potential

Potential activity of Fe(III) reducing bacteria was assayed using synthetic amorphous Fe oxyhydroxide. It was synthesized and washed according to Lovley and Phillips (1986b), dispensed to brown glass vials, purged with nitrogen and autoclaved. Five ml of synthetic Fe

oxyhydroxide slurry were combined with 1 ml of wet sediment in an anoxic chamber (95:5 $N_2:H_2$ atmosphere), mixed and analyzed for HCl-soluble Fe(II). After 6 days incubation at 20°C in the dark, accumulation of Fe(II) was determined. Duplicates poisoned with $HgCl_2$ were prepared from some samples to check for possible abiotic Fe(III) reduction.

RESULTS

Geochemical Environment

Lake Niemegk

The geochemical environment of the sediments in the acidic Lake Niemegk (Fig. 2) and the neutral Lake Doebern (Fig. 3) differed apart from pH values mainly in the extent of temporal variability. The pH values in Lake Niemegk sediment differed widely with depth and time of sampling, ranging from pH 2.7 up to pH 5.5. The sediment surface showed the lowest pH values throughout. Prominent pH peaks were found in different depths.

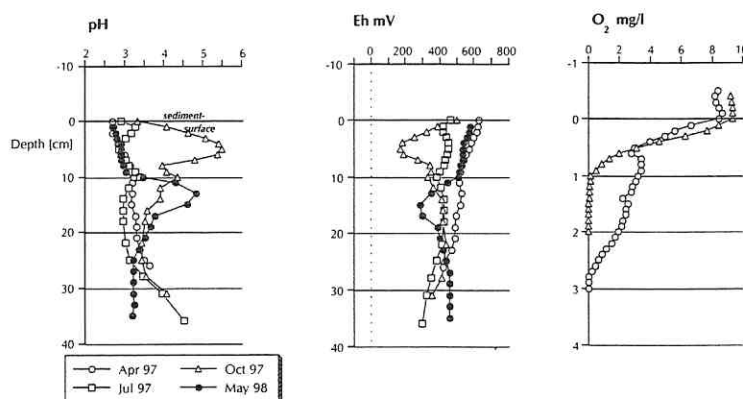


Fig. 2: Distribution of pH, E_H and O_2 in the sediments of Lake Niemegk.

The pH maximum of 5.5 was reached in October in 5 cm depth and with the peak value of pH 4.8 in May 1998 at a depth of 12 cm. Profiles of redox potentials (E_H) in the sediments were generally negatively correlated to pH profiles. Values ranged from 175 mV to 631 mV. Oxygen profiles were only measured in April and October 1997, since the water above the sediment surface was already anoxic in July 1997 and May 1998. In April 1997 oxygen penetrated the sediment to a depth of 28 mm, the discontinuity at 7 mm indicates disturbance during sampling. Oxygen penetration in October reached 11 mm depth.

Lake Doebern

In contrast to Lake Niemegek sediments, pH, E_H and oxygen profiles in Lake Doebern sediments indicate a temporally more uniform geochemical environment (Fig. 3). However, geochemical parameters changed with depth. The pH values ranged from pH 6 to 7. Below the minima at the sediment surface pH increased towards a maximum. Like in Lake Niemegek, the redox and pH profiles were negatively correlated. The absolute values of E_H were generally lower and reached negative values. Depths of oxygen penetration were comparable to Lake Niemegek sediments. In July 1997 and May 1998, water above the sediment was also almost anoxic.

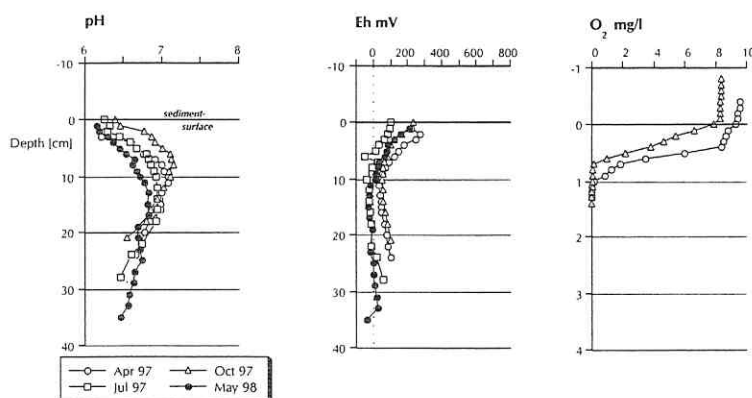


Fig. 3: Distribution of pH, E_H and O₂ in the sediments of Lake Doebern.

Solid Phases

With sediment traps exposed in May and November 1998 high accumulation rates of 21.5 and 28.1 g m⁻²d⁻¹ were determined. Analysis of solid phases of the sediment trap and the sediment materials revealed similar geochemical compositions for both lakes (Fig. 4). However, differences were found especially in the distribution of minerals. Lake Niemegek sediments possessed more homogeneous solid phases compared to Lake Doebern.

In general, water content of the sediments was high (up to 99%). Below 24 cm sandy overburden materials prevailed which were distinguished from authigenic sediments by their lower water contents and a markedly different composition. Porosities calculated after Richards (1962) were between 0.97 and 0.99. Extremely high Fe contents between 200 and 400 mg/g of dry weight (DW) were typical. The more or less uniformly distributed Al and Si contents are very low compared to natural lake sediments.

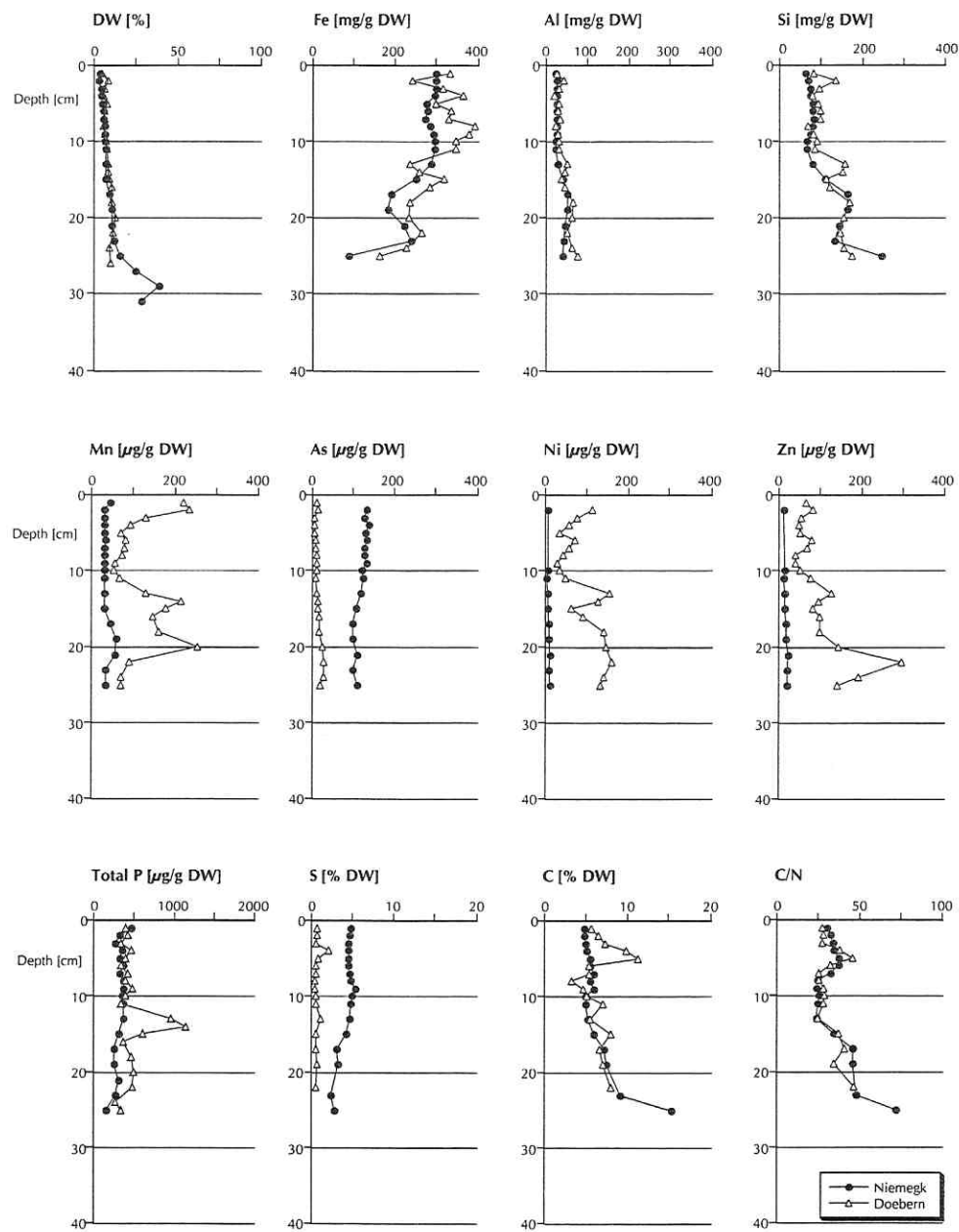


Fig. 4: Distribution of dry weight (DW), Fe, Al, Si, Mn, Zn, Ni, TP, C, S and atomic ratio of C/N in the sediments of Lake Niemegek and Lake Doebern (4/97).

The distributions of P and C with average contents of 500 µg/g DW and 5-10% DW were similar in both sediments. C/N ratios showed values between 25 and 75 and increased with depth.

Differences in elemental composition between the two lakes existed with respect to the metals Mn, Ni, Zn and As. Mn, Zn and Ni were enriched in the solid phases of Lake Doebern sediments compared to Lake Niemegk. Contrarily, As was found in 10 times higher concentrations in Lake Niemegk sediment. Whereas in Lake Niemegk metals were homogeneously distributed throughout, Lake Doebern exhibited distinct zones of metal enrichment. Zones enriched in Mn occurred near the surface and in deeper layers. Lake Niemegk sediments were 7 times higher in sulfur content over the whole depth.

Mineralogical composition of the two sediments was similar with respect to their main constituents. The sediments consisted mostly of poorly and better crystalline Fe hydroxides. The poorly crystalline Fe hydroxides could not be identified unequivocally. RDX studies indicated the presence of schwertmannite in Lake Niemegk sediments. Among the crystalline Fe hydroxides, goethite was detected in varying proportions in both sediments. Quartz, kaolinite, illite, muscovite and orthoclase were also identified as main components (Fig. 5). In deeper layers of Lake Doebern sediment up to 10% siderite was detected.

Pore Waters

Pore water profiles of Fe, SO_4^{2-} , SRP, DOC and heavy metals in both lakes are displayed in Fig. 6 and 7. In some cases the scales chosen for Lake Niemegk and Doebern diagrams differ to facilitate process-oriented comparison of results.

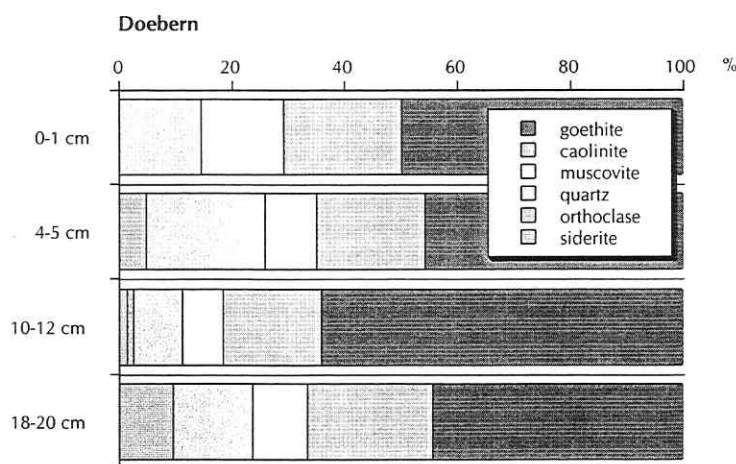


Fig. 5: Distribution of crystalline minerals in sediments of Lake Doebern.

Pore waters are characterized by extremely high Fe and SO_4^{2-} concentrations with even higher concentrations in the acidic milieu of Lake Niemegk. Mn and DOC concentrations were also elevated compared to pore waters of natural lakes, whereas SRP concentrations were relatively low. Total Fe determination in pore waters from May 1998 demonstrated that all Fe in pore water was Fe(II). Pore water chemistry differed markedly between Lake Niemegk and Lake Doebern and between sampling dates for each lake. Within 3 months, absolute concentrations of most analytes changed more than 100%. The overlying water possessed equal or lower concentrations than the corresponding pore waters for all parameters, therefore no gradient directed into the sediment existed. The steepest gradients at the sediment surface occurred for Fe and SO_4^{2-} .

Lake Niemegek

In Lake Niemegek sediments, pore waters were extremely enriched in Fe and SO_4^{2-} with concentrations of 700–4800 mg/l for Fe and 2800–18000 mg/l for SO_4^{2-} . Minima always occurred at the sediment surface, and concentrations increased with depth. Profiles of Fe, SO_4^{2-} and SRP from the same sampling date were positively correlated. In addition to changes in absolute concentrations, direction and steepness of gradients in the profiles varied with time.

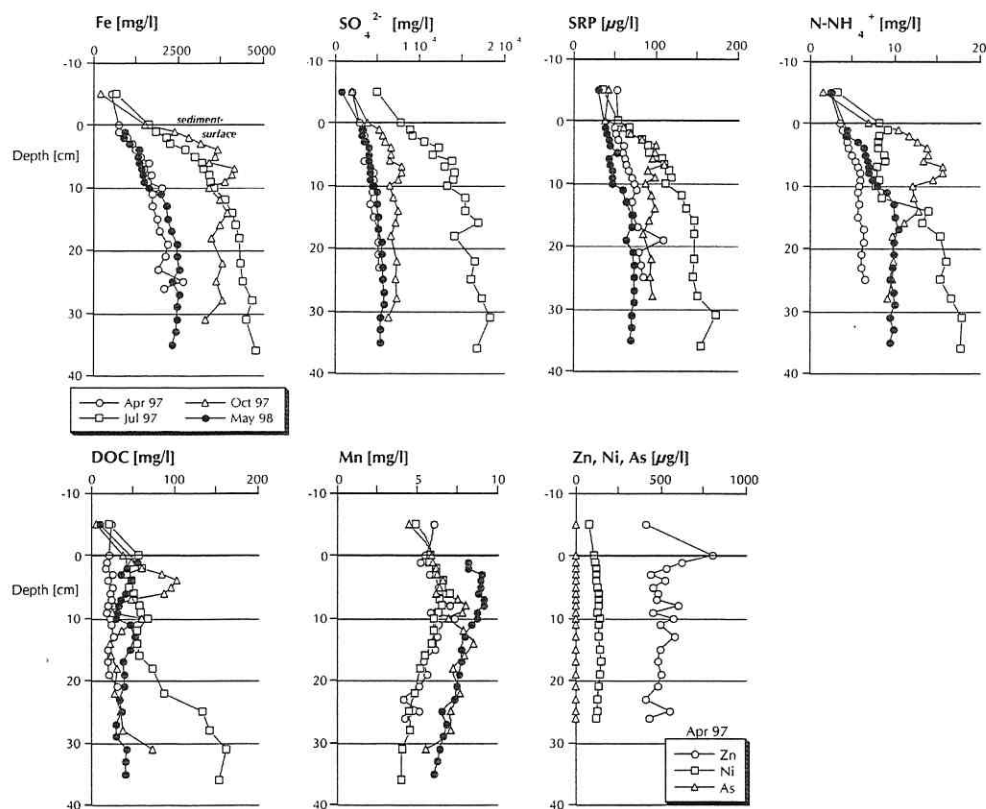


Fig. 6: Pore water profiles of Fe, SO_4^{2-} , SRP, N-NH_4^+ , DOC, Mn, Zn, Ni, and As in Lake Niemegek sediment.

In April 1997, Fe and SO_4^{2-} profiles appeared as almost linear functions with fairly constant gradients. Profiles of other sampling dates possessed zones with steep gradients directed towards the sediment surface. In general, steeper gradients occurred in upper sediment layers whereas below 10-15 cm gradients were relatively weak. Conspicuous increases in concentration were found in October 1997 in the top 10 cm and in May 1998 around 4 and 11 cm depth. DOC varied considerably with time and depth. Distinct zones with DOC peaks with values up to 100 mg/l coincide with strong increases in Fe, SO_4^{2-} and SRP as well as with changes in pH and E_H . Nitrate concentrations were very low (20-130 $\mu\text{g/l}$, data not shown). Mn profiles remained more constant with time. There was a general trend for all profiles with higher concentrations in the upper parts and continuous decrease with depth. The heavy metals Zn, Ni and As were only measured in pore waters in April 1997. Contrary to the solid phase investigations, Zn reached the highest concentrations and As the lowest. The distribution of Ni and As with depth was very homogeneous. Zn showed a maximum at the sediment surface and was more variable with depth.

Lake Doebern

Pore water profiles for Lake Doebern are displayed in Fig. 7. Iron and SO_4^{2-} concentrations were remarkably lower compared to Lake Niemegk, and no overall correlation between Fe, SO_4^{2-} and SRP concentrations was found. Absolute concentrations and depth patterns differed strongly between sampling dates. Fe concentrations reached up to 880 mg/l with minima at the sediment surface. When bottom water was oxic, Fe was almost depleted. Generally, Fe increased in the upper 10 cm of the sediment to form gradients with different steepness. Sulfate profiles showed two different trends with depth: in April and October 1997 and May 1998 an increase up to 2000 mg/l in the upper 10 cm was observed, whereas in July 1997 SO_4^{2-} decreased to 1200 mg/l.

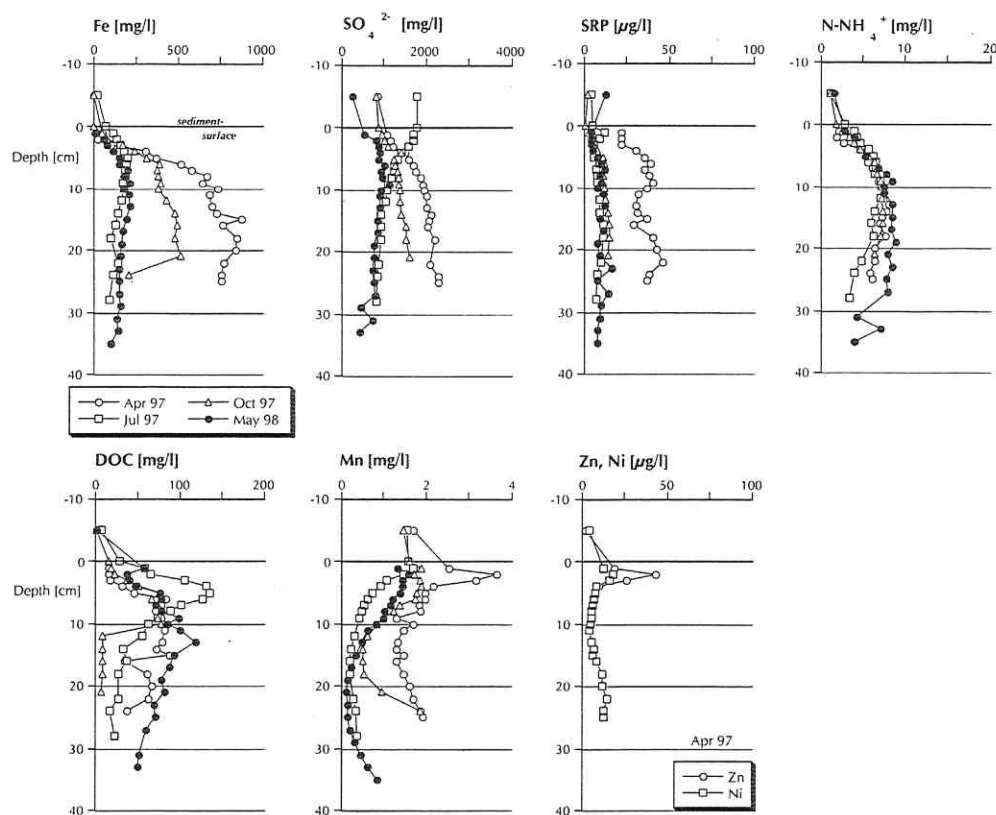


Fig.7: Pore water profiles of Fe, SO_4^{2-} , SRP, N-NH_4^+ , DOC, Mn, Zn, Ni, and As in Lake Doebern sediment.

SRP concentrations were very low ($\sim 50 \mu\text{g/l}$), and profiles were very similar except April 1997. Nitrate-N was present only in $\mu\text{g/l}$ concentrations in all samples (data not shown). The profiles of N-NH_4^+ were almost identical for all sampling dates in the top 10 cm with an increase to 10 mg/l. Like in the Niemegek Lake sediments, DOC concentrations showed prominent temporal variation with formed peak values up to 135 mg/l. Manganese, Zn and Ni profiles showed some similarities

to Lake Niemegek profiles with the concentration peaks below the sediment surface. As was not detected in pore waters.

Bonded Forms

Fig. 8 shows the relations between ascorbate- and dithionite-soluble Fe(III). According to Kostka and Luther (1994), Ferdelmann (1988) and Lord (1980), ascorbate dissolves poorly crystalline and dithionite dissolves better crystalline Fe(III) oxides. The ratio of these Fe(III) fractions markedly decreased with depth in both lake sediments, but in Lake Niemegek absolute values were almost 10 times higher. In upper layers poorly crystalline Fe(III)oxides dominated in both sediments, but with increasing depth the ratio changes and better crystalline phases became more prominent. Sediment trap material mainly consisted of poorly crystalline Fe(III) oxides.

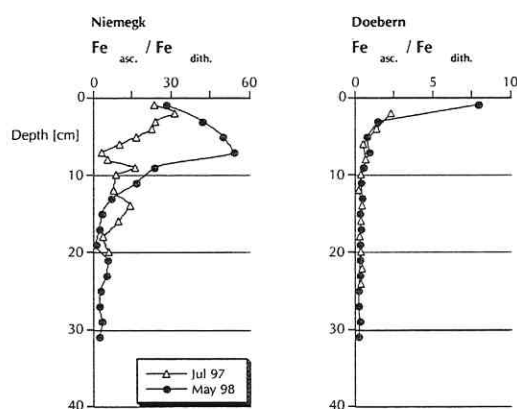


Fig. 8: Ratio of ascorbate -soluble iron and dithionite-soluble iron in Lake Niemegek and Lake Doebern sediments; note different scales. Iron is interpreted as ferric iron from amorphous and crystalline iron oxides, respectively (Lord, 1980; Ferdelmann, 1988).

In both sediments only low sulfide mineral contents were detected. Tab. 2 shows AVS and CRS content of selected sediment layers. While in Lake Niemegek low but uniformly distributed CRS contents were found, no AVS was detected. In Lake Doebern sediment, AVS occurred in the middle part of the core, but not above or below. CRS content increased with depth. Hydroxylamine-reducible Fe ('microbially available') per g fresh weight was extremely high (125-450 $\mu\text{mol/g}$ wet sediment, Fe(II) not subtracted) and generally increased with depth (Fig. 9). However, there was considerable irregularity in deeper layers. HCl-soluble Fe(II) correspond with concentrations in pore waters.

Tab. 2: Distribution of AVS and CRS in sediments of Lake Niemegek and Lake Doebern.

(AVS, CRS : x = 0-10; xx = 10-100; xxx = 100-1000 $\mu\text{g/g}$ wet sediment; n.d. not detectable)

	Depth [cm]	AVS	CRS
Niemegek	2-3	n.d.	xx
	6-7	n.d.	xx
	14-15	n.d.	xx
	25-27	n.d.	xx
Doebern	2-3	n.d.	x
	6-7	x	xx
	14-15	xx	xx
	25-27	n.d.	xxx

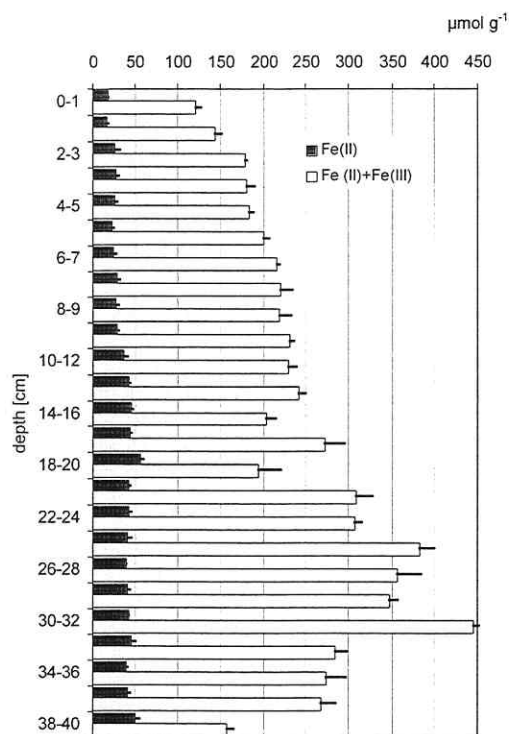


Fig. 9: HCl-soluble Fe(II) and hydroxylamine-reducible Fe(III) in Lake Niemegk sediment with depth, 05/98 (wet weight). Error bars are standard deviations of triplicates.

Fe(III) Reduction

Measurements of potential Fe(III) reduction revealed two zones of high activity, 6-9 and 14-18 cm. Some Fe(II) was also produced in poisoned controls, but this was always far below biotic values (Fig. 10). Since abiotic reduction of Fe(III) can occur in the presence of Hg^{2+} under acidic conditions (E. Roden, pers. comm.), these values were not subtracted in further calculations.

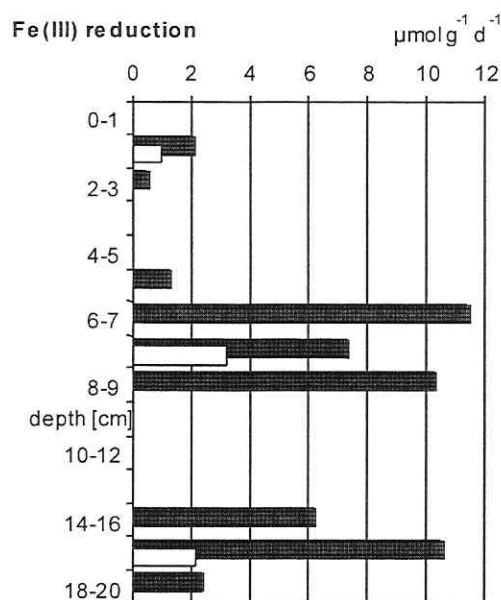


Fig. 10: Potential Fe(III) reduction from laboratory incubations with Lake Niemegk sediment (05/98). White bars show Fe(III) reduction in poisoned controls.

DISCUSSION

Lake Niemegk

Sedimentation

The high accumulation rates determined with sediment traps would result in 1.5 and 2.2 cm per month of newly deposited sediment when assuming a porosity of 0.98 resembling the upper sediment layers (0-5 cm). On the basis of this rate and average porosities, after 6 years 60 cm of sediment would have accumulated. This might be an overestimation because the sediment traps present additional centers for crystallization and precipitation of Fe oxyhydroxides on their surfaces. Since sedimentation rates vary with time, we might have also determined maximum

rates. Acidic lakes in Lusatia possessed lower accumulation rates of max. $11.7 \text{ g m}^{-2} \text{ d}^{-1}$ (Peine, 1998).

Material from the sediment traps was similar to the upper sediment layers with respect to geochemistry and mineralogy. Similar to other acidic mining lakes (Frieze et al., 1998; Peine, 1998; Peiffer and Peine, 1998; White et al., 1989), the suspension-like sediments of Lake Niemegk mainly consist of floc-like poorly crystalline Fe(III) oxides. The proportion of accumulated Fe is generally lower in the sediments of older lakes with similar acidity (Frieze et al., 1998; Peine, 1998).

The Fe:S ratio and geochemical milieu point to a likely formation of schwertmannite. However, since its crystalline structure could not be unequivocally confirmed by either RDX analysis, the presence of schwertmannite could not be proven with certainty. This uncertainty is partly due to the inhomogeneity of the sample material; the precipitates may have formed under non-stationary conditions. Because of this uncertainty we performed geochemical equilibrium calculations with PHREEQC (Parkhurst, 1995) of pore water data. From this we obtained solubility lines for different Fe hydroxides versus pH and $\log \text{Fe}^{3+}$ activity (Fig. 11). Sediments of upper layers from 0-8 cm depth are determined by the solubility of schwertmannite, which can be precipitated under these conditions as a characteristic Fe(III) oxide of acidic lakes (Bigham et al., 1990; 1996a) and has already been detected in other acidic waters (Schwertmann et al., 1995; Bigham et al., 1996b; Peine, 1998; Peine et al., 2000). Other minerals like quartz, kaolinite, muscovite were carried into the lake from the surrounding overburden by erosion and landslides.

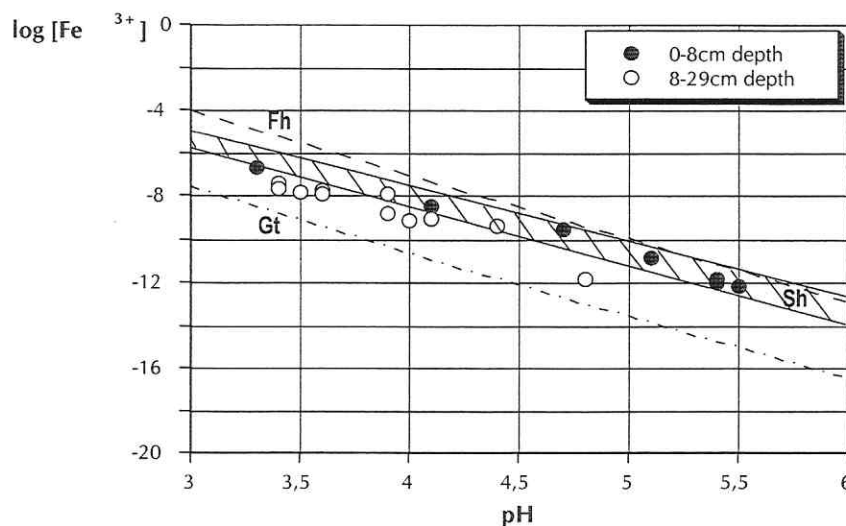


Fig.11: Plot of Fe^{3+} activity against pH for pore water data (Niemegk) with solubility lines of goethite (Gt), ferrihydrite (Fh) and solubility window of schwertmannite (Sh), calculated after Bigham et al. (1996b) and log K values of 1.4, 4.89, 18.0.

Fe(III) reduction and Fe(II) oxidation in sediments

The variability of the geochemical milieu of Lake Niemegk sediments with time and space indicates different geochemical reactions of varying intensity. In these sediments decomposition of organic matter by microbial Fe(III) reduction is a dominant biogeochemical process. This reaction appears to be controlled by a large supply of bioavailable carbon and poorly crystalline Fe(III)hydroxides in conjunction with favourable nutrient conditions for microorganisms.

In October 1997 and May 1998 dissolution of Fe(III) oxides by microbial Fe(III) reduction must have occurred. Whereas in October 1997 one Fe(III) reduction zone was detected geochemically, in May 1998 two separate zones of this reaction were detected by geochemical and microbiological methods. In these zones mineralization of organic matter is indicated by

increasing DOC and NH_4^+ concentrations. Likewise high concentration gradients of Fe(II) and SO_4^{2-} suggest a dissolution of schwertmannite by Fe(III) reduction. As this is an acid-consuming process, the pH value generally increases. In May 1998 in the upper zone the pH value remained at a constant low level. Hence this is evidence of an additional acid-producing process. The distinct zones with pronounced pH peaks are accompanied by increased microbial Fe(III) reduction potential and higher abundance of Fe(III) reducing and sulfate reducing bacteria (Wendt-Potthoff and Langner, 2001).

Whereas the site of reaction of the reductive zones was geochemically located at 4 and 10 cm, the microbiological methods located them each 2 cm deeper in the sediment. This might be caused by a sampling artifact. Geochemically, the pore water serves as an indicator for Fe(III) reduction, microbiologically it is the bacteria mainly associated with the particulate phase. The liquid phase of the suspension-like sediment could have been forced upwards during sampling by the stopper pressed into the core liner from below.

To compare potential Fe(III) reduction rates from the microbial activity assays with in situ rates, reduction rates were calculated from Fe fluxes for the layers with pronounced increase in Fe concentration (4-5, 10-11 cm, Fig. 12). For this purpose, a basic concentration gradient was determined for the layers directly below (Fig. 13). This basic gradient influences the flux in the two active layers by diffusive transport. Subtraction of this basic gradient yields the concentration gradient caused by Fe(III) reduction. From this the Fe fluxes in the two zones caused by microbial Fe(III) reduction were calculated on the basis of molecular diffusion with a diffusion coefficient $D_0\text{Fe}^{2+}$ (7.5°C) after Li and Gregory (1974). The reduction rates calculated from diffusive fluxes of reduction zones were 2.3 and 2.7 $\mu\text{mol cm}^{-3} \text{ d}^{-1}$.

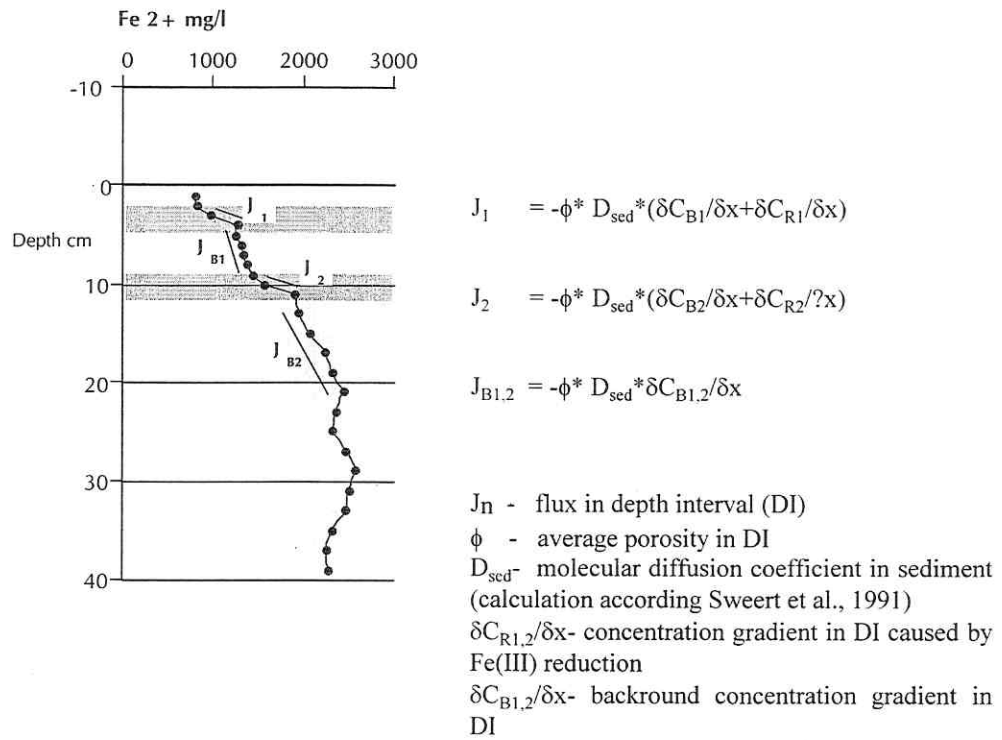


Fig. 12: Distribution of Fe(II) in pore waters of Lake Niemegk sediment (5/98) and calculation of diffusive fluxes.

Blodau et al. (1998) found considerably lower Fe(III) reduction rates (max. $150 \text{ nmol cm}^{-3} \text{ d}^{-1}$) for an acidic mining lake in Brandenburg with similar total Fe content of the sediment. Peine (1998) also determined lower in situ rates (max. $250 \text{ nmol cm}^{-3} \text{ d}^{-1}$) in an acidic lake in Lusatia. Since potential rates determined by microbiological assays were in the same order of magnitude, our results seem realistic. Potential activity rates determined in the laboratory have often been reported to overestimate in situ activity.

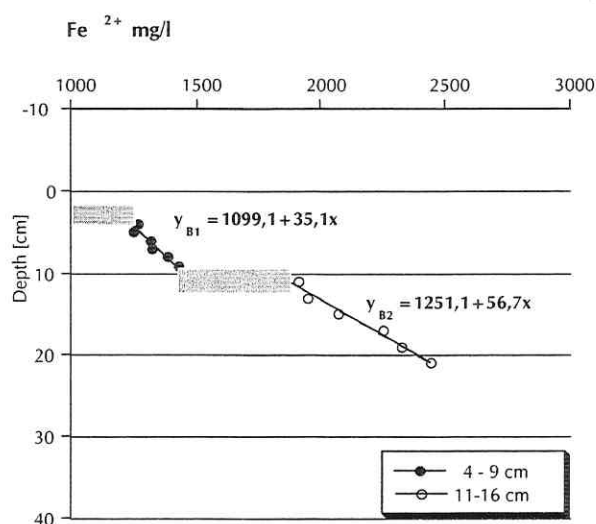


Fig. 13: Calculated straight lines in pore water profiles of Fe(II)concentration to determine background gradients of Fe(II)concentration.

Possible reasons are temperature effects, artificially high concentrations of electron donor or general limitations of batch experiments (Chapelle and Lovley, 1990; Phelps et al., 1994; Murphy and Schramke, 1998). In our assays, temperature was 20°C and hydrogen from the atmosphere of the anaerobic chamber was present as a potential additional electron donor, which both might have stimulated microbial activity. Contrarily the dilution with 5 volumes of Fe hydroxide slurry could have posed some stress on the microbial community.

The relatively high Fe(III) reduction rates may have been caused by two effects. Firstly, organic carbon supply in lake Niemegek sediment is higher than in other acidic mining lakes. Woelfl (2000) observed sporadic proliferation of microalgae to very high abundance which represent an easily degradable carbon source after sinking to the sediment. Secondly, Lake Niemegek is

characterized by a relatively high inorganic nutrient supply. Lovley and Phillips (1986a) found slightly elevated reduction of amorphous Fe hydroxides in the presence of adsorbed P. Moreover, similar geochemically and microbiologically determined rates indicate that the main transport process in the sediment is indeed molecular diffusion and not advective transport. Otherwise, the geochemically determined rates would have been at least tenfold higher than those determined microbiologically.

With reductive dissolution of Fe hydroxides, adsorptively bound SRP is also released. Extraction of P fractions after Psenner et al. (1984) have shown that a large fraction of total P is bound to Fe hydroxides (Langner and Friese, 2001).

However, below the reductive zones, poorly crystalline Fe(III) oxides decrease in favor of better crystalline ones with increasing pH. This could be the result of ongoing dissolution of the microbially available poorly crystalline oxides. Lovley and Phillips (1986b) demonstrated the preferred reduction of poorly crystalline versus better crystalline oxides. Elevated DOC concentrations connected with Fe(III) reduction result from two overlapping processes. Firstly, easily degradable organic compounds like freshly deposited algal material are decomposed, releasing metabolic products into solution. This is supported by increased microbial biomass near the surface and in the lower Fe(III) reduction zone (Wendt-Potthoff and Langner, 2001). Secondly, a large fraction of the organic carbon must be bound to Fe(III) hydroxides which is released into solution upon their reductive dissolution. The preferred adsorption of humic substances to Fe(III) oxides has been proved in numerous studies (Vermeer et al., 1998a; 1998b; Ali and Dzombak, 1996; McKnight et al., 1992; Tipping, 1981). In extracts for dissolution of Fe compounds, high DOC contents (up to 30% of total carbon in the respective sediment sample) were measured. Fe fractionation studies and stable isotope signatures performed by Nohlen (1999) also indicated binding of large amounts of organic matter originating from lignite to

Fe(III) oxides. Presumably these are humic substances derived from the lignite in the underground, which had diffused to recently deposited sediment from below and adsorbed there. These substances could have contributed to the high Fe(III) reduction rates. Recent work of Benz et al. (1998), Scott et al. (1998) and Lovley et al. (1996, 1998) showed that the presence of humic substances stimulates microbial Fe(III) reduction by acting as electron shuttle.

The reduced Fe diffuses to the sediment surface and there Fe(III) hydroxides are precipitated due to the oxidation of Fe^{2+} by thiobacilli (Wendt-Potthoff and Langner, 2001) and dissolved oxygen. This acid-producing reaction leads to a decrease in pH and in Fe, SO_4^{2-} and SRP concentrations due to co-precipitation. Since Fe(II) concentrations do not reach zero at the sediment surface, a large fraction is transported to the lake bottom waters and precipitated there.

The consumption of oxygen in lake sediment during oxic conditions in bottom water must be mainly caused by Fe(II) oxidation. In contrast to many other investigations oxygen consumption by oxidation of organic matter seems much less important. A rough calculation of the degradation rate of organic matter by O_2 in the sediment (assuming an oxygen penetration of 10 mm and complete O_2 consumption by organic matter degradation) shows that this is more than 10 times lower than by Fe(III)reduction.

Fe(III) conversion by mineral transformation

Another important reaction which strongly influences the geochemical milieu in the sediments as an acid-producing process is the mineral transformation of schwertmannite to goethite. The continuous about fivefold increase in crystalline oxides per cm sediment depth in the upper 15 cm also points to a permanent transformation of Fe(III) oxides due to aging and/or other reactions. The mineral schwertmannite as characteristic Fe(III) oxide of acidic waters is meta-stable and is

transformed into goethite with changing pH (Bigham et al., 1996b). The detection of goethite in deeper layers, although not as the dominant Fe(III) phase, indicates the relevance of this process. The results of geochemical equilibrium calculations for pore waters (Fig. 11) further support this. Pore waters of greater depths cluster predominantly between the solubility window of schwertmannite and the solubility line of goethite. Indices for the transformation of schwertmannite to goethite were also found in an acidic mining lake in Lusatia by Peine (1998). In upper sediment layers schwertmannite was found, below (4-8 cm) goethite was detected. However, the transformation process was confined to a narrower zone, which might be connected to the lower sedimentation rates and lower sediment water content in that lake.

Heavy metals

The heavy metals Zn and Ni occur mainly dissolved in pore water under acidic conditions, whereas As is mainly bound to the solid phase. Because of the non-sulfidic conditions heavy metals can be sorbed to Fe(III) oxides. An explanation for the different behaviour of Zn, Ni and As could be their different charge which influences adsorption. Surface charge measurements indicated that the sediment probably carries positive charges at pH 3 (Meiwirth, 1997). Calculations of Zn, Ni and As species distribution with PHREEQC (Parkhurst, 1995) for these geochemical conditions showed that only As occurred as predominantly negatively charged species (95% as H_2AsO^-) and is therefore readily sorbed. According to Bigham et al. (1990), As can be integrated in the tunnel structure of schwertmannite. Elevated Zn concentrations near the surface are probably due to release into solution coupled to organic matter decomposition.

Lake Doebern

Sediments of the neutral mining lake, Lake Doebern, also consist mostly of flocc-like Fe oxyhydroxides. Whereas in upper layers (0-5 cm) poorly crystalline forms predominate, deeper layers contain up to 65% goethite which is a stable oxide under the prevailing geochemical conditions.

Like in Lake Niemegek sediment the oxidation of organic matter by Fe(III) reduction is of considerable importance and seems to determine the diagenesis of the sediments. Below the sediment surface the pH profile and elevated concentrations of DOC and N-NH_4^+ in pore waters provide evidence of Fe(III) reduction. Furthermore, this process is indicated by the authigenic formation of siderite which has accumulated up to 10% of total Fe in deeper layers. During formation of ferrous minerals carbonates and sulfides compete for dissolved Fe^{2+} which leads to low Fe concentrations in pore water. The large fractions of siderite suggest that precipitation of this mineral is preferred. Schinzel et al. (1993) also found in laboratory studies on early diagenetic reactions involving Fe oxyhydroxides that carbonates were preferentially formed. Sulfide formation was of minor importance due to missing diffusive sulfate transport. In other mining lakes in Germany, only sulfidic Fe(II) phases in minor amounts have been detected (Frieze et al., 1998; Peine and Peiffer, 1998; Blodau et al., 1998). Low redox potentials (up to -50 mV) and detection of AVS ($\text{H}_2\text{S} + \text{FeS}$) in July 1997 point to organic matter decomposition under sulfate reducing conditions. AVS was localized in the zone of maximum pH and minimum E_H values. Increasing FeS_2 concentrations with depth also support H_2S generation and subsequent pyrite formation. However, this sulfide enrichment with depth was small compared to that of Fe(II) carbonate. Since there was no sulfate limitation, H_2S production rates might have been low. Alternatively, sulfide precipitation could have been prevented by rapid reoxidation. Studies of

Lake Niemegk and of other mining lakes (Meier, 2001) show that sulfide oxidizing bacteria are abundant to high sediment depths despite oxygen depletion. Probably Fe(III) oxides can serve as electron acceptor for sulfide oxidation.

The relative constance of geochemical parameters (pH, E_H , $N-NH_4^+$) with time indicates a stable milieu. Degradation of organic matter does not seem to be exclusively determined by Fe(III) reduction. Sulfides detected in the sediment suggest the occurrence of microbial sulfate reduction.

Under oxic conditions in the overflowing lake bottom water Fe(II) diffusing upwards is oxidized in the upper cm of the sediment and precipitated as poorly crystalline hydroxide. This leads to Fe enrichment near the surface. Similar to Lake Niemegk, Fe oxidation and hydroxide precipitation contribute significantly to O_2 consumption and proton release, respectively.

Pore water profiles of manganese show a dissolution zone below the sediment surface, most notably in April 1997. In deeper layers the profiles indicate precipitation of Mn minerals. Unfortunately, because of their low concentrations, these phases could not be identified by RDX analyses. Given the suboxic conditions and formation of authigenic siderite, Mn most likely also precipitated as carbonate, as it was the case in laboratory experiments of Schinzel et al. (1993).

If the heavy metals Zn and Ni (which in contrast to Lake Niemegk sediment had solid phase concentrations up to 200 $\mu\text{g/g}$ DW) occurred adsorbed or sulfidic remains unclear. However, concentration peaks below the sediment surface in April 1997 indicate dissolution of Zn and Ni not associated with Fe oxides. This could be explained by rapid release from other freshly deposited particles. Hamilton-Taylor et al.(1996) and Reynolds and Hamilton-Taylor (1992) postulated for another lake that Zn was derived from planctonic algae.

Geochemical Modeling

In order to verify the postulated main biogeochemical processes of Fe turnover in acidic Lake Niemegk sediments, geochemical modeling with CoTRem (Hensen et al., 1997; Landenberger et al., 1997, Landenberger, 1998; Adler et al., 2000a, 2000b) was performed. Depth profiles of pH, Fe^{2+} , SO_4^{2-} and NH_4^+ concentrations in pore water were modeled to demonstrate the interaction of these processes and their dominant influence on the system. The program CoTRem (Landenberger, 1998) couples geochemical reactions with transport processes. Four key processes were defined for our modeling: (1) the oxidation of dissolved Fe^{2+} at the sediment surface and precipitation of Fe(III) hydroxide as schwertmannite; (2) the oxidation of easily degradable organic matter by Fe(III) reduction using schwertmannite as an acid-consuming process; (3) the transformation of schwertmannite to goethite (through dissolution of schwertmannite); (4) Equilibrium to goethite (as an acid-producing process); (5) the input of Fe^{2+} , SO_4^{2-} , NH_4^+ and H^+ by diffusive transport from deeper layers (upper and lower boundary conditions, Tab. 3).

Firstly, the dependence of the geochemical parameters and intensity of reactions (2) and (3) were tested by modeling. Secondly, the model was applied to the geochemical situations of October 1997 and May 1998. We attempted to fit modeled data to measured geochemical parameters, verifying validity of processes by pH modeling.

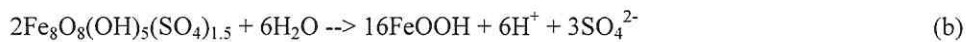
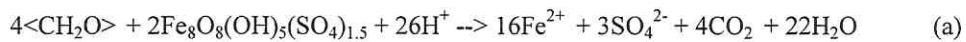
Fig. 14 shows the distribution of pH value, Fe^{2+} , SO_4^{2-} and NH_4^+ concentrations in pore water, and transformation rates of schwertmannite during oxidation of organic matter and during goethite formation.

Tab. 3: Upper and lower boundary conditions defined by modeling of the distribution of pore waters in October 1997 and May 1998.

	October 1997		May 1998	
Tiefe [cm]	0	31.5	0	31.5
pH	2.92	3.40	2.95	3.36
Fe ²⁺ [mmol]	4.11	75.00	4.11	50.00
SO ₄ ²⁻ [mmol]	25.20	80.00	20.20	60.00
NH ₄ ⁺ [mmol]	0.19	0.40	0.14	0.55

In this general modeling approach we assumed that reaction rates of (2) and (3) decreased with depth. The model showed that with constant reaction rates inside one sediment layer, pH values increased in the upper zone (0-10 cm) and reached an endpoint value of 5.3 after 55 days. In deeper layers a much lower pH value of 3.2-3.5 was reached. In contrast to pH, Fe²⁺, SO₄²⁻ and NH₄⁺ concentrations continued to increase.

The general modeling showed that the most important regulating factor for pH values below the sediment surface was the ratio of both reactions involving schwertmannite: (a) organic matter oxidation and (b) transformation of schwertmannite into goethite.



To reach an equilibrium between proton consumption and release at pH 3, transformation of schwertmannite with a composition of $\text{Fe}_8\text{O}_8(\text{OH})_5\text{SO}_4)_{1.5}$ into goethite would have to be 4.3 times as fast as schwertmannite reaction during oxidation of organic matter. This results in a ratio of 0.23 (reaction (a):(b)). In the upper part of the profile where pH increased with time, the ratio exceeds 0.23. In the deeper part the ratio is close to 0.23, so that no pH increase results from biogeochemical reactions. Here, because of changing concentration gradients, molecular diffusion mainly drives pH development. The ratio of reactions (a) and (b) is not linearly correlated to pH value, since other parameters like the proposed equilibrium with goethite also influence pH. Furthermore modeling shows that at the sediment surface (0-1 cm), where ratio (a):(b) is at maximum, pH is additionally controlled by H^+ influx from lake bottom water. However, the turnover rates described in (a) and (b) and their ratio generally dominate pH development.

If the turnover rate of schwertmannite with organic matter is varied by 10%, dramatic effects on pH will result. After an increase of 10% for 18 days after 91 days with the originally proposed rate, pH further increases to 5.6 and 3.6 in the upper and lower zones, respectively. A 10% reduced rate changes the ratio of processes in favor of proton release, so that pH decreases again. This demonstrates that pH reacts very sensitive towards varying turnover rates.

If the results from geochemical and microbiological analyses are used to model pore water profiles of a given sampling date, definition of a baseline for the different concentrations is crucial. This baseline is determined by diffusive transport of solutes with groundwater. Since true baseline profiles are unknown, assumptions are made which reflect natural conditions as close as possible. In Fig. 14, 15 and 16 the starting profiles represent the baselines. Furthermore, the preferred zones of Fe(III) reduction with measured turnover rates were defined. Rates of schwertmannite transformation into goethite decrease with depth and were adjusted in a way that modeled profiles approximated measured concentrations in a given time frame.

Fig. 15 displays model results of profiles from October 1997. Rates of Fe(III) reduction in the upper part of the sediment were assumed to be similar to calculated rates in May 1998. With respect to pH, Fe^{2+} and SO_4^{2-} concentrations, measured profiles could be fairly well reproduced by modeling. Within 91 days, the pH profile reached an equilibrium, meaning no further temporal changes occurred in a range of days. This indicates that reactions and transport processes were balanced with respect to H^+ concentrations.

Fe^{2+} and SO_4^{2-} concentrations approximated measured profiles after 91 days. The distribution of NH_4^+ differed slightly from measured values. This could be explained by the composition of

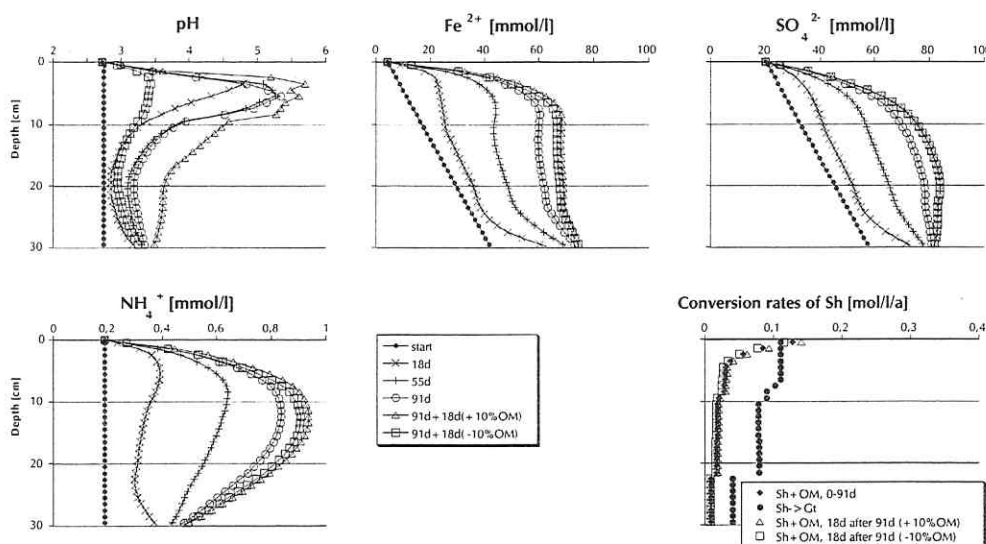


Fig.14: With CoTReM simulated profiles of pH, Fe^{2+} , SO_4^{2-} and NH_4^+ in pore waters after 18, 55 and 91 days, calculated with conversion rates of schwertmannite (Sh) for a) decomposition of organic matter with schwertmannite (Sh+OM) and b) for the transmission of schwertmannite to goethite (Sh->Gt). Additionally after 91 days for a) two runs were carried out with 10% reduced and increased conversion rates (duration 18 days).

organic matter in the sediment. A C/N ratio of 13.25 was chosen for modeling assuming a significant contribution of lignite decomposition products to organic matter. However, the real C/N ratio of organic matter remains unknown.

Fig. 16 displays modeling of profiles from May 1998. Zones of Fe(III) reduction were defined to be localized between 4-8 and between 11-14 cm with turnover rates of $2 \mu\text{mol cm}^{-3}\text{d}^{-1}$ (similar to calculated data). In the remaining sediment layers Fe(III) reduction rates were assumed to be tenfold lower.

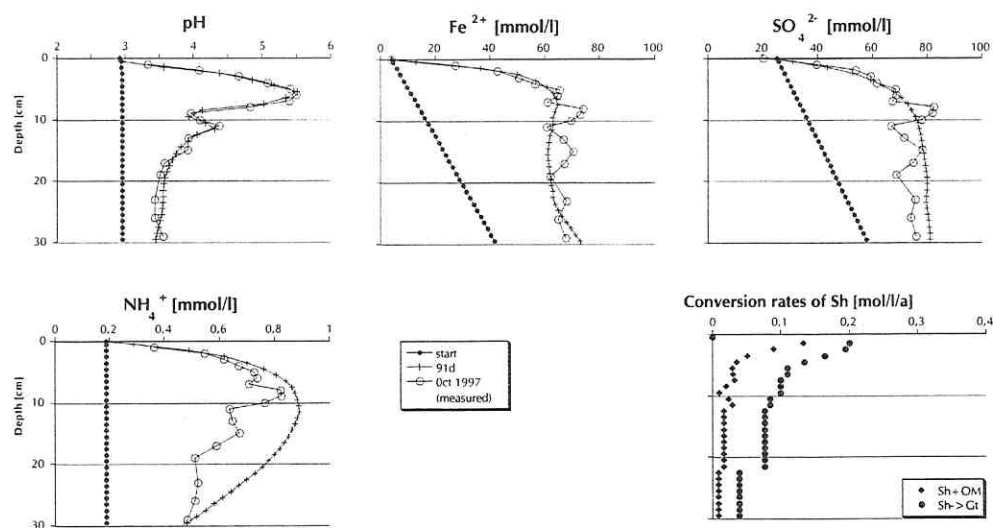


Fig.15: Measured and with CoTReM simulated profiles of pH, Fe²⁺, SO₄²⁻, NH₄⁺ in pore waters for October 1997, calculations after 91 days with conversion rates of schwertmannite (Sh) for a) decomposition of organic matter with schwertmannite (Sh+OM) and b) for transmission of schwertmannite to goethite (Sh->Gt).

Zones of schwertmannite transformation into goethite seemed to be directly coupled to Fe(III) reduction zones. In the lower zone the elevated pH values were reached faster because of a slightly higher ratio of the two schwertmannite turnover rates. In addition, pH development in the upper zone was buffered by H^+ influx from lake bottom water.

The pH values in the lower zone continued to increase and approximated the measured profile after 2 weeks. However, an equilibrium similar to that found with October data was not reached after this time.

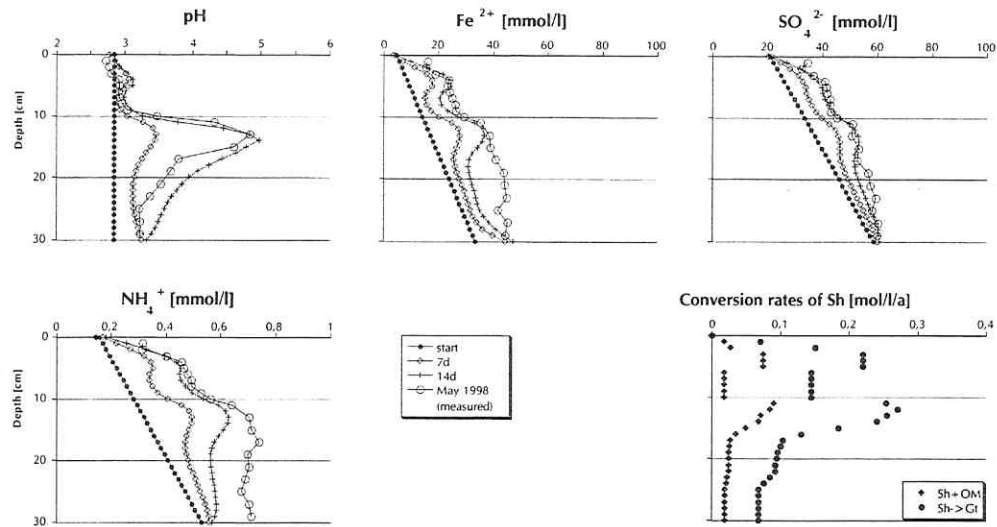


Fig.16: Measured and with CoTReM simulated profiles of pH, Fe^{2+} , SO_4^{2-} , NH_4^+ in pore waters for May 1998, calculations after 91 days with conversion rates of schwertmannite (Sh) for a) decomposition of organic matter with schwertmannite (Sh+OM) and b) for transmission of schwertmannite to goethite (Sh->Gt).

Modeled Fe^{2+} concentrations show the development of plateaux at the upper boundaries of the Fe(III) reduction zones, but values below these zones do not fully reproduce the measurements. Since baselines of concentrations can only be defined on an assumptive basis and exact information on the temporal continuity of processes is not available, modeled concentrations profiles can to some extent differ from measured values.

Overall, modeling of the geochemical situations of October 1997 and May 1998 revealed that the investigated sediments were strongly influenced by external diffusive input from deeper sediment layers and that the observed processes are highly variable over time. In general, however, concentration profiles as modeled with CoTReM showed a very good fit to the measured data suggesting that the assumed processes make a good approximation to natural conditions.

CONCLUSIONS

We investigated the sediments of a neutral and an acidic lake of similar age in the same mine. Although their sediment matrix was similar, they showed distinct differences in bonding forms of heavy metals and formation of authigenic minerals (sulfides vs. carbonates). They also differed with respect to geochemical stability with time. The pH sensitivity of organic matter degradation and schwertmannite transformation caused a geochemically instable system in the acidic lake sediment.

Geochemical and microbiological methods revealed a distinct zonation of iron transformation processes in the acidic lake sediment. Two Fe(III) reduction zones were evident, the lower being due to heterotrophic Fe(III) reduction accompanied by net alkalinity generation.

These geochemical and microbiological studies provided a good basis to define processes for geochemical modeling. Observed pH profiles could be well reproduced by modeling with CoTReM, assuming organic matter decomposition with Fe(III) reduction and the transformation of schwertmannite into goethite as the most important geochemical processes. The model also confirmed the temporal instability of geochemical parameters in this sediment.

When modeling the October and May situations no steady states were reached. Iron and sulfate concentrations continue to increase with ongoing organic matter decomposition. In contrast, pH reaches a relative equilibrium in October as well as in May. Modeling revealed that the measured situations are only transient states and are highly influenced by temporal variations in transformation rates and boundary parameters.

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2.2

Mesocosm studies for the investigation of phosphorus retention in sediment during and after the flooding of lignite mining lakes

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Abstract -Flooding of acid mining lakes with river water causes large quantities of phosphorus to sorptively bind to iron hydroxides which, through re-dissolution from the sediments, can be released back into the pore water thereby entering the water column. To investigate P-retention in the sediments incubation experiments of sediment cores from an acid mining lake were carried out, with which conditions during and after the flooding were simulated. The sediment cores were flushed regularly with acidic and neutral river water, of which samples were regularly taken during the incubation. Additionally, the influence on a carbon-enriched sediment and mud enriched with $\text{Fe}(\text{OH})_3$ was examined. The sediment cores were removed from the incubation system after several weeks. Geochemical investigation of pore waters and solid phases were performed.

If a good stock of bioavailable carbon, almost the entire P sorbed to the $\text{Fe}(\text{OH})_3$ was converted to vivianite. The turnover rate is determined in particular by the pH development in the sediment, whose constituency is influenced predominately by the bottom water pH, Fe(III) reduction and the mineral transformations from schwertmannite to goethite. Equilibrium calculations with PHREEQC (Parkhurst, 1995) indicate that in the pore water the soluble reactive phosphorus (SRP) concentrations are controlled by its conversion to vivianite and therefore decrease with rising pH values in the range 4 to 7. After 8 weeks the SRP flux from bottom water under acidic conditions

($0.2 \text{ mmol m}^{-2} \text{ d}^{-1}$) was an order of magnitude higher than the flux from neutral bottom water. A high portion of iron in the sediments of the acid mining lakes (indicated by high atomic ratios Fe/SRP of pore waters (>100) and solid phases (60-150)) guarantees a high conversion of dissolved SRP to Vivianite and also through sorptive fixation to iron hydroxides.

INTRODUCTION

Until a few years ago large quantities of lignite coal were mined in the eastern part of Germany. The extraction of sediment and dumping of waste material from the acid mining operations caused the oxidation of pyrite, the majority of which was found in the sediment layers. The groundwater levels of extensive areas surrounding the extraction sites were lowered. Consequently, atmospheric oxygen penetrated into the sediment zones formerly saturated with water, allowing the oxidation to take place. This status was preserved even after termination of the mining operation. Several techniques exist to prevent the further oxidation in the ground (Schultze et al., 1999 and references therein). One possibility is the flooding of the mining lakes with groundwater. This, however, results in oxidation products being transported by the groundwater from the ground into the mining lake, giving its water very acidic pH values and high contents of Fe, SO_4^{2-} and heavy metals, as is the case in many mining lakes found in Lusatia (Peine, 1998; Friese et al., 1998). Another possibility to halt the oxidation process in the ground is to flood the mining lakes with river water. This, however, may increase the potential of eutrophication of the mining lake waters since most rivers in the area have a high nutrient content. In particular, a high phosphorus content in the river waters presently flooding mining lakes causes the lakewaters to become hypereutrophic (Hupfer et al., 1998; Klapper and Schultze,

1995). This leads to the development of large algal blooms, whose decomposition in the sediment results in anoxic conditions in the hypolimnion, intensifying release of phosphorus and other materials such as metals from the sediment into the water column and degrading the water quality. Both the phosphorus content directly in the water and the phosphorus pool in the sediments are of equal importance for this degradation process of the water quality in the mining lakes. During the flooding of the mining lakes with river water a large portion of the phosphorus transported into the mining lake is adsorbed to iron hydroxides and precipitates out of the water. Investigations by Jensen and Thamdrup (1993) and Psenner and Puscko (1988) stress the importance of the role iron hydroxides play in binding phosphorus in pore water. Many investigations show that this iron-phosphorus bond is very unstable and that the phosphorus easily re-dissolves into the pore waters through the reduction of iron hydroxides during the early stages of diagenesis and is transported via diffusion into the water column (e.g. Eckert et al., 1997; Jensen et al., 1995; Nürnberg, 1988; Baccini, 1985). Other studies show that the material transformations in the sediments are controlled by the iron cycle (Emerson and Widmer, 1978; Nriagu and Dell, 1974). For iron-dominated systems, Nriagu and Dell (1974) found ferrosferric hydroxyphosphates and Vivianite to be the most stable minerals, respectively, under oxidized and reduced conditions in the sediments. Other studies carried out in sulphate-rich system suggest that the two cycles can be decoupled through the formation of iron sulphide (Kleeberg and Kozerski, 1997; Caraco et al., 1993). The results from Roden and Edmonds (1997) indicate the immobilization PO_4^{3-} under Fe(III) oxide-reducing conditions, but that a PO_4^{3-} release takes place when sediment iron compounds are converted to iron sulphides.

The hitherto phosphorus investigations in mining lake sediment systems were carried out under relatively stable conditions (with the exception of the oxygen content in the ground). The

objectives of this research are to study the effects of extreme changes of pH in the bottom water (ranging between 3 and 7) and the effect of increased P and POC sedimentation on the phosphorus retention in the sediments. Furthermore, the uniqueness of these sediments due to their extremely high iron content allow important questions pertaining to the phosphorus-iron dynamics to be investigated: i) What P-fraction in these sediments can be re-dissolved by Fe (III) reduction during the degradation of organic material? ii) What quantity and forms of the released phosphorus is reprecipitated to the sediments? iii) What influence does the pH in bottom water have on the P-conversions? iv) What is the magnitude of the diffusive flux of phosphorus from the sediments to the overlying water column and to the deeper sediment layers? vi) Do the P binding forms change in the deeper sediment layers?

Since the mining lake sediments also consist of a large portion of microbial and highly available iron hydroxides (Friese et al., 1998; Langner et al., 2001; Peine, 1998), the mining lake sediments form an autogenic system dominated by the iron cycle, which dominates the phosphorus transformations. Hence, it is particularly important to examine the phosphorus retention in the sediments in juxtaposition with the carbon and iron transformations. For this purpose, experiments were carried out on incubated sediment cores from the mining Lake Niemegek (Goitsche) to investigate the phosphorus retention for a period of six months.

MATERIALS AND METHODS

Study Site

The former open-pit mine Goitsche is situated in Central Germany where several mining lakes of different size remain after termination of the mining operation. Water from the rising groundwater table has seeped into some of the mining lakes and either neutral or acidic pH values can be measured in the collected water. The mining lakes are being flooded with water from the Mulde river. Before the water is discharged into the mining lakes, its quality is first ameliorated by allowing it to pass through a reservoir, which acts as a clarifier removing many nutrients (up to 25% phosphorus, Hupfer et al., 1998) and other pollutants by sedimentation. However, the substances removed from the river water accumulate in the reservoir sediments and can re-enter the water cycle through the early diagenetic processes. A single channel diverts the river water to one of the Goitsche mining lakes and due to their interconnectivity, the mining lakes are consecutively being filled to their prescribed water level of 75 m.a.s.l. Once all mining lakes have been filled, diversion of river water through the pit system will continue until the groundwater table has attained a mean steady state with the pit water level. In order to ensure that the few oxidation products from the surrounding ground do not enter the pit water, the flooding is carried out at a fast enough rate so that the groundwater flow occurs in the direction away from the mining lakes. Fig. 1 shows the expected morphology of the pit system. Prognoses of the mining lake water quality indicate relatively low pH values for the water for the entire flooding duration but neutral values thereafter when only occasional river water diversions are required for water replenishment (Limnological expertise, 1999).

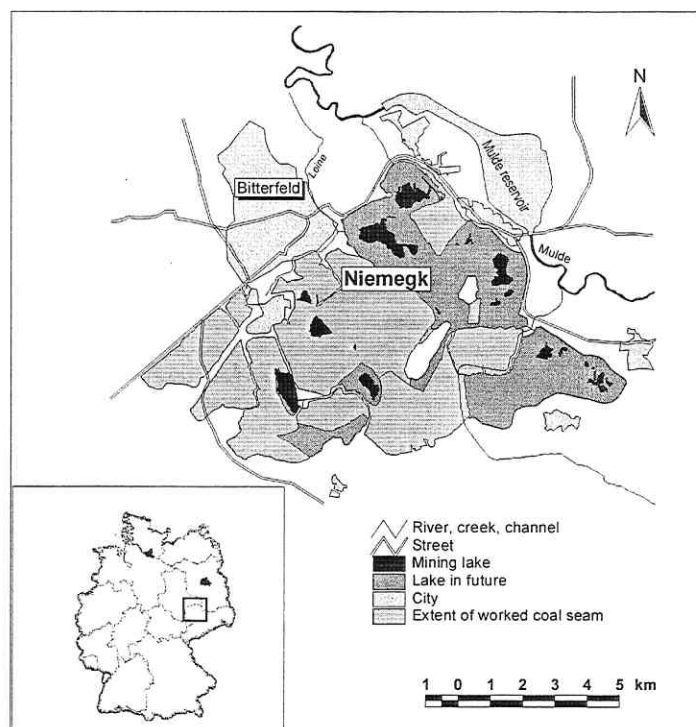


Fig. 1: Map of study site.

The sediment cores for laboratory experiments were taken from the acidic Niemegeksee (part of the Goitsche pit system) in May 1998. Langner et al. (2001) describe the geochemical and microbiological analyses carried out on the core samples to determine the early diagenetic processes in these very young sediments. The suspension-like sediments consist largely of iron hydroxides flakes. The dominant biogeochemical processes that occur in the sediments and that contribute substantially to the control of the pH are: (1) the oxidation of dissolved Fe^{2+} from the pore water at the sediment surface and the precipitation of ferric oxide; (2) the transformation or

oxidation of easily available organic material by means of microbial Fe(III) reduction in ferric oxides; (3) the transformation from schwertmannite to goethite during the dissolution of schwertmannite; (4) the transport of Fe^{2+} , SO_4^{2-} , NH_4^+ and H^+ and other substances from the groundwater into the mining lake water (Langner et al., 2001). Processes (2) and (3) particularly contribute to the pH dynamics in the sediments. Furthermore, very high transport rates via molecular diffusion could be determined due to the extremely steep density gradients in the pore water and the high porosity of the sediments ($\eta \approx 0.97$). In contrast to 'normal' lake sediments, the pH of the bottom water has a large influence on the upper sediment layers, in regard to strong diffusive entry of H^+ from the bottom water.

Field Sampling

The laboratory experiments were carried out on sediment cores, which were extracted from the Niemeck mining lake in May 1998. A gravity corer with 9 cm diameter polycarbonate tubes was used for the extraction. This system allows the sediment cores to remain undisturbed for transport to the laboratory. Before and during the flooding of the mining lakes, sediment traps were placed in Niemeck Lake and Mühlbeck Lake for 2 weeks, after which they were removed and their collected sediments analysed.

Mesocosm Design

The sediment cores were placed into the experimental apparatuses in the laboratory. Table 1 gives an overview of the incubation conditions of the sediment cores, which were kept constant for predefined time periods. Great care was taken to match the laboratory conditions as closely as possible with those found in the field during and after the flooding. Effects due to the groundwater during the flooding, could not, however, be simulated. Water drawn from the Mulde river outlet briefly prior to commencement of the experiment was continuously passed in a cycle over the undisturbed sediment cores (Fig. 2). The water volume corresponded to a water column of one meter above the sediment core. Experiments with colour tracers determined the flow velocity of the water over the sediment to be within the cm/s range as would be found at the bottom of the mining lake. Three cycles, each with three sediment cores, were run in parallel. After 8, 16 and 24 weeks one sediment core of each cycle was removed and examined. Fig. 3 shows a schematic diagram of one such cycle. A cooling unit kept the sediment cores and the cycled water at 10 and 14° C, respectively. Oxygen and pH of the cycled water was continuously regulated, but it was not possible to keep the water free of O₂ during the 8 to 16 week period of the experiment. N₂ was emitted into the water for 4 weeks during the last stage (16 to 24 weeks) of the experiment in order to keep it clear of O₂. The pH of the water was kept at a preset value using a feedback controlled simulation unit (Fig. 3) (pH controller, PR12, DR. A. KUNTZE), which regulated the addition of NaOH or HCL to the water with an attached dosing pump. The river water was stored in a reservoir in which the water was continuously stirred and its pH and O₂ were regulated. After the 8 and 16 week periods the water was replaced with fresh river water. In order to simulate a large phosphorus pool in the sediment, whose behaviour and depth distribution was to be studied over a certain time span, a single dose of 12 mg P cm⁻² was

administered to the sediment. The dose consisted of 80 ml of $\text{Fe}(\text{OH})_3$ sludge (344 mg/g DW) with adsorbed phosphate (prepared sensu Lovley and Phillipps (1986) and was applied to the sediment core surfaces in two cycles (Experiment 2 and 3).

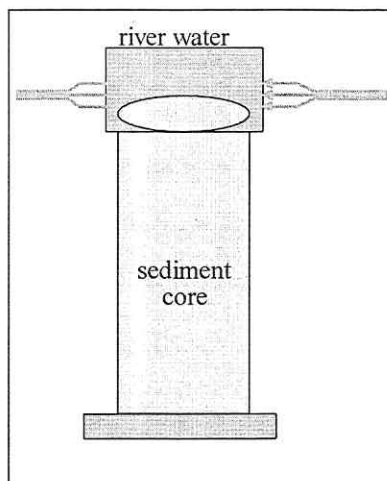


Fig. 2: Sediment core with flow cell. The sediment surface was overflowed by river water.

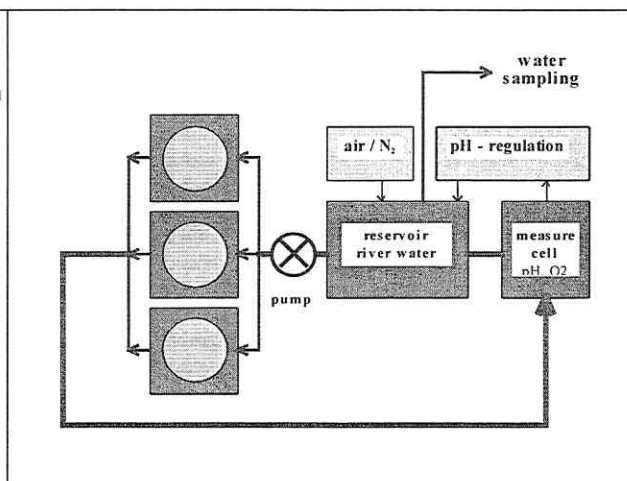


Fig. 3: Scheme of sediment incubation system.

At the beginning of the experiment, 15 ml of dead algal material was added to the upper 2 cm layer of the sediment core in order to simulate an increased sedimentation from algae. An addition 9 ml was added after the 8 and 16 week periods. This quantity of algal material correspond to a simulated POC sedimentation of $750 \text{ mg m}^{-2} \text{ d}^{-1}$ for the first 8 weeks and $450 \text{ mg m}^{-2} \text{ d}^{-1}$ for the remaining time. These rates are comparable to the mean and maximum POC sedimentation rates of eutrophic and hypereutrophic lakes (e.g. Molongoski and Klug, 1980; Hupfer et al., 1995; Henschel, 1995; Bernasconi et al., 1997). The algae, which consisted mostly

of blue-green and green algal species, were collected in April 1998 from the Mulde reservoir with a plankton net (mesh size > 20µm) and kept frozen until applied to the core surfaces.

Sampling and Analysis

During the entire experiment, samples of the water overflowing the sediment surface were taken regularly for analysis of SRP, Fe and SO_4^{2-} . After each replacement of the water with newly acquired Mulde river water, samples were taken every 3 or 4 days and thereafter in weekly intervals. Unfortunately, several mishaps occurred during the first few weeks and the water needed to be exchanged several times.

After removal from the cycle, the cores were immediately sampled in an inert gas (argon) atmosphere (see Langner et al. (2001) for details). Pore water extraction by centrifugation and analysis are also described by Langner et al.(2001). Table 2 gives an overview of the analytical methods used. Determination of the P bound formations on the i) sediment cores of the experiment, ii) freshly-extracted (initial) sediment from Lake Niemegek, iii) settling seston, and iv) sediment from pH-neutral Doebern Lake (for comparative studies) within the same open pit lake system, were carried out using a sequential extraction scheme according to Hupfer et al. (1995) and Psenner et al. (1984) with slight modifications. A large portion of P in the NaOH fraction was expected to come from the newly formed vivianite (Psenner et al., 1984). The residual P was taken as TP in the residual material (P digestion). With the exception of the initial sediments only the TP contents in the extracts were determined. Since the adsorbed P in the applied sludge corresponded to SRP and the algal material consisted of 6mg P/g DW, which is equivalent to 0.6 % of the total supplemented P, TP concentrations can be equated to SRP. For the P extractions, 1 to 2 g of fresh sediment were sampled in an inert gas atmosphere and filled in

polyethylene centrifuge tubes, which were then weighed and filled with 20 ml of oxygen-free extraction solutions. Samples were taken from 0-5 cm and > 5 cm core depths. After this the samples were extracted using a shaker (23 rpm/min) and then centrifuged (10 min, 3800 rpm/s). The separated liquid was then passed through a 0.45µm cellulose acetate filter using a Schleicher & Schell syringe filter. The sediment was washed with 20 ml of their respective extraction solution. The P contents of the centrifuged and filtered washing solution, as well as the extracted solution were analysed. The entire procedure was repeated on the remaining sediment with the respective extraction solution.

The TP concentrations in the filtered extractants were determined according to DEV (1992). The TP contents of the NaOH extraction solution were measured using an ICP-OES, due to their problems with photometric analysis. As a check of both the TP contents and the Fe:P ratios in the sediments, freeze-dried sample material of the initial sediment and the upper 5 cm sediment of the experiment were additionally analysed by means of RFA (VARIO EL, ELEMENTAR). In order to detect the formation of vivianite, selected freeze dried samples of the sediment surface (0-1 cm) of each core were examined using Mössbauer spectroscopy. Total and organic C and S were determined with elemental analyzer (VARIO EL, ELEMNTAR).

RESULTS AND DISCUSSION

P - Releasing Zones

The initial sediments consisted predominately of poorly crystallized ferric hydroxides (Langner et al., 2001), which was reflected in the high iron content of 160-350 mg/g DW in the solid phase (data not shown). Two reducing zones in these sediments, where SRP release occurred, were found at depths of 3-4 cm and 10-12 cm (Langner et al., 2001). The depth distribution of the SRP content in the pore water of the initial sediments is positively correlated with that of iron (Langner et al., 2001).

The concentration curves of SRP in the pore waters of the initial sediments and the sediment after 8, 16 and 24 weeks incubation time are shown in Fig. 4. In general, SRP concentration peaks in conjunction with Fe(III) reduction were found only in the upper centimetres of the sediments for

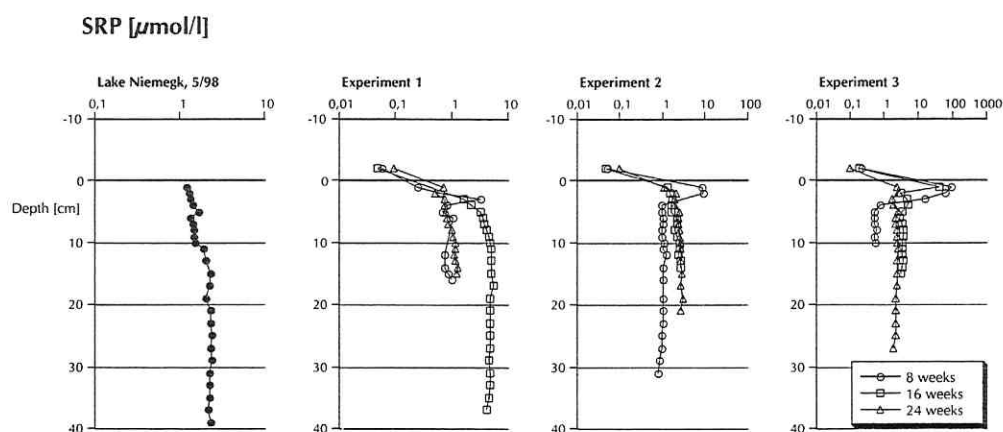


Fig. 4: Pore water profiles of Lake Niemegek and experiment 1, 2 and 3 after incubation time of 8, 16, 24 weeks.

all incubation cycles. After 8 weeks the absolute contents in Experiments 1, 2 and 3 differed by an order of magnitude, which can be attributed to the different incubation conditions in which different processes predominate. At the end of the experiment (after 24 weeks), all SRP concentration distributions in the pore waters had matched those of the initial sediments. It could be observed that in all incubation sediments below the release zone, the SRP concentrations in the pore water over time remained in the same order of magnitude (1-10 $\mu\text{mol/l}$). This may be the result of the 'stable' Fe-hydroxide pools in the sediments that, according to Jensen and Thamdrup (1993), control the equilibrium between adsorbed SRP and pore water SRP.

In Experiment 1, with neutral pH conditions in the overflowing water, a well-pronounced SRP release zone was formed at 3 cm after only 8 weeks. The microbial investigations did not reveal a prevalent ferric reduction zone throughout the entire incubation period in the sediments of this experiment, which could be explained by the missing carbon source (Wendt-Potthoff and Langner, 2001).

The sediment pore waters with added C and P (Experiments 2 and 3) showed pronounced SRP peaks under the sediment surface (0-3 cm) after 8 weeks, which correlate with steep Fe density gradients in the pore water and detected ferric reductions zones (Wendt-Potthoff and Langner, 2001). The results are indicative of the SRP release due to re-dissolution processes, in which organic substances are degraded under $\text{Fe}(\text{OH})_3$ -dissolution by microbial ferric reduction.

However, the content of the SRP peaks of Experiment 3 are an order of magnitude higher than Experiment 2 with pH-neutral overflowing water. Since, according to Wendt-Potthoff and Langner (2001), the ferric reduction rates in this zone are similar to those found in the reduction zones of the sediments with pH-neutral overflowing water, it appears as if the higher SRP concentrations correlate closely with the relatively small pH values in the sediments. The pH

controls the ion activity product of iron phosphate minerals such as vivianite, and thus influences the SRP concentrations in the pore waters. This will be discussed in greater depth in Section 3.4.

P-Fluxes at the Sediment Surface

In general, the P-flux at the water-sediment interface is determined by the porosity of the sediments, the diffusion coefficients and the concentration gradients of the different P species. Which species are present in the pore waters depends primarily on the geochemical environment conditions. Fig. 5 shows the distribution of the P-species calculated with PHREEQC (Parkhurst, 1995) as a function of pH at high Fe^{2+} and SO_4^{2-} content (according to the composition of the pore water). In acidic conditions, the P distribution in the pore waters consists of 3/5 of the $\text{FeH}_2\text{PO}_4^+$

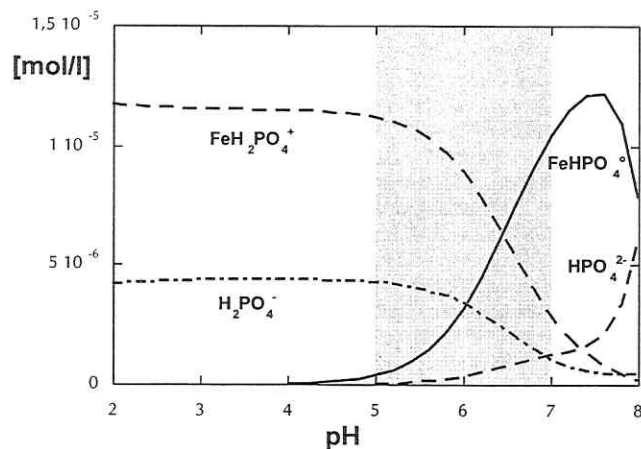


Fig. 5: PHREEQC calculations of P-Species distribution subject to pH with typical Fe^{2+} and SO_4^{2-} pore waters concentrations of acid mining lake sediments ($\text{Fe}^{2+} = 30 \text{ mmol/l}$, $\text{SO}_4^{2-} = 30 \text{ mmol/l}$, $\text{PO}_4^{3-} = 0.016 \text{ mmol/l}$).

species and 2/5 of the H_2PO_4^- species. At pH values between 5 and 7, which were present in the upper sediment layers of the examined sediments, the distribution of the species changes substantially toward FeHPO_4° .

In this regard, the P-flux can strongly change when drastic pH fluctuations within a few centimetres in the depth profile occur. The distribution of the P-fluxes on the individual species, apart from the species concentrations or their gradients, is determined by their molecular diffusion coefficient. This varies with the P-species present by approximately 30% in the following order: $\text{H}_2\text{PO}_4^- > \text{HPO}_4^{2-} > \text{FeHPO}_4^\circ$. Since no value for the molecular diffusion coefficient for $\text{FeH}_2\text{PO}_4^+$

was found in the literature its value was estimated for the flux calculations. The diffusive flux was calculated according to Fick's first law of diffusion modified for porous media:

$$J = -\phi * D_{\text{sed}} * (\delta C / \delta x)$$

where:

ϕ = porosity in depth interval

D_{sed} = molecular diffusion coefficient in sediment

$\delta C / \delta x$ = concentration gradient

Sweert et al. (1991) calculated the diffusion coefficients in fresh water sediments of high porosity using:

$$D_{\text{sed}} = D_0 / (-0.73 * \phi + 2.17)$$

where D_0 is the molecular diffusion coefficient (Li and Gregory, 1974; Furrer and Wehrli, 1996), corrected for in situ temperature of 10°C and $I = 0.005$.

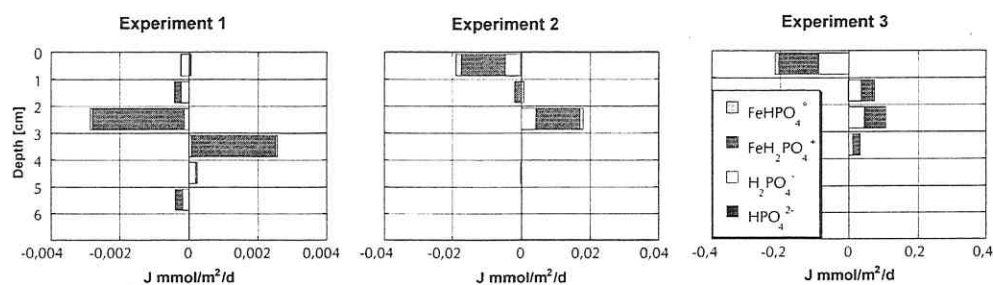


Fig. 6: Calculated diffusive fluxes of P-species of the experiments after 8 weeks incubation time (positive flux - in deeper sediment layer, negative flux - in upper sediment layer or bottom water).

The P-fluxes changed during the incubation experiments particularly in the upper sediment layers, due to the different incubation conditions. Changes occurred in the flow amount of P, the distribution on the individual P-species, as well as its function with time.

The calculated SRP fluxes in the upper 5 centimetres of the sediments of the three approaches were highest after 8 weeks incubation and varied in concentration by an order of magnitude higher as did the concentration in the pore waters ($0.003 - 0.2 \text{ mmol m}^{-2} \text{ d}^{-1}$) (Fig.6). The SRP fluxes in the incubation experiments with pH-neutral overflowing water were considerably less than calculated SRP fluxes from pore water data from other eutrophic lakes (Kleeberg and Kozerski, 1997; Eckert et al., 1997; Baccini, 1985; Emerson, 1976; Emerson and Widmer, 1978). For acidic overflowing water, the fluxes range from similar to less than the values found in the aforementioned literature.

Under pH-neutral overflowing water conditions the SRP fluxes reduce, relative to the pore water concentrations, much faster than with acidic overflowing water. Whilst the SRP fluxes with neutral overflowing water become very small already after 16 weeks, the SRP fluxes of Experiment 3 adjusted to the values found in the 'control' Experiment 1 only after adjusting the

pH of overflowing water to pH-neutral conditions (16-24 weeks). The SRP fluxes from the sediment surface to the water were of similar magnitudes compared to those found in the deeper sediment layers.

Overflowing Water

The SRP content, which is transported into the overflowing water, is derived from the SRP flux at the sediment surface (see Section 3.2). Since the SRP contents in the overflowing water during the incubation experiments do not correspond to the expected values calculated from the SRP fluxes, the higher flux rates and processes occurring in the overflowing water must initially determine the concentrations.

The concentration distribution of SRP and Fe in the overflowing water can be clearly assigned to the concentration pattern of the different pH and O₂ conditions in the water (Fig. 7).

The continual precipitation of Fe-hydroxides in the overflowing water and the adsorption of P on their surfaces rapidly reduces the SRP contents under O₂ saturated and neutral pH conditions to concentrations to approximately the 0.02 mg/l level. Within four weeks almost all of the P in the water and the P transported from the pores into the water was bound by the Fe-precipitation. A SRP fixation of up to 29 mmol/m² in the overflowing water shows (Fig. 8) that a high P enrichment can be obtained in the sediment through settled suspended matter.

Under acidic conditions in the overflowing water the initial fluxes of Fe and SRP must be higher than the oxidation or precipitation rates at the sediment surface. The SRP contents begin to decrease substantially only after 5 weeks in the overflowing water, if the rising Fe concentrations level off to approximately 20 mg/l, indicative of a constant precipitation of Fe-hydroxides.

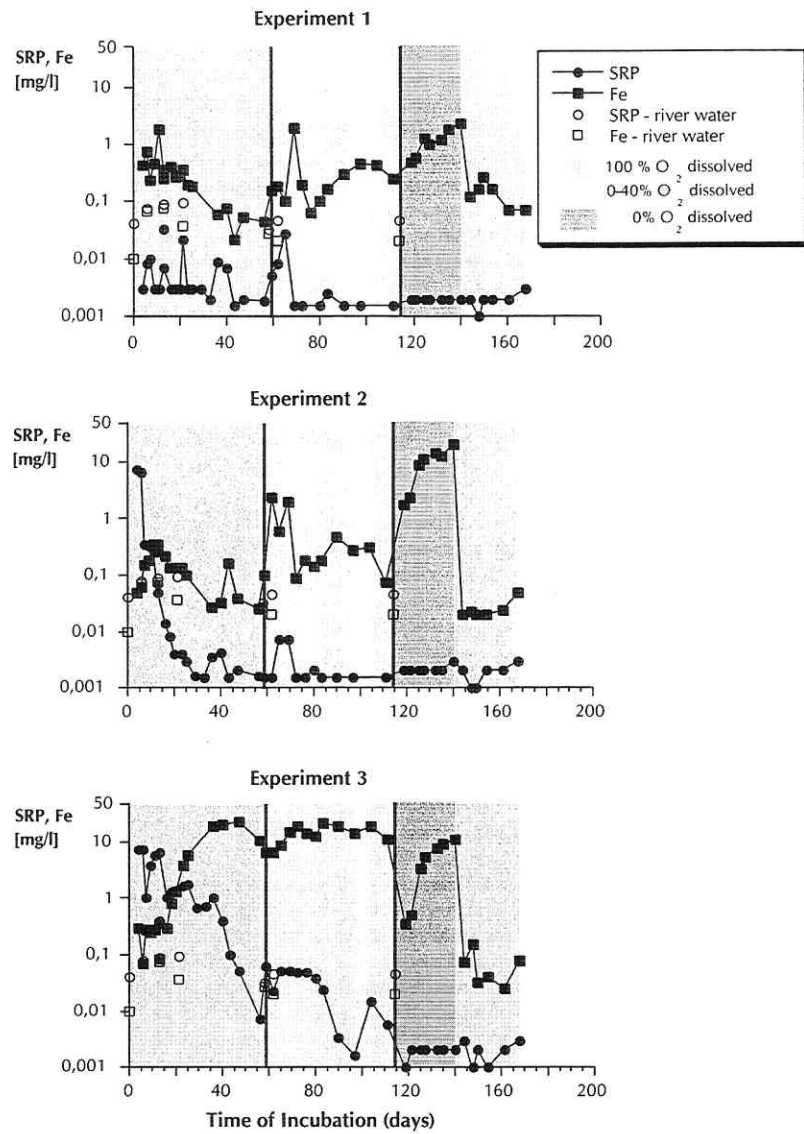


Fig. 7: Distribution of SRP and Fe in the overflowing water of experiment 1, 2 and 3 during the incubation.

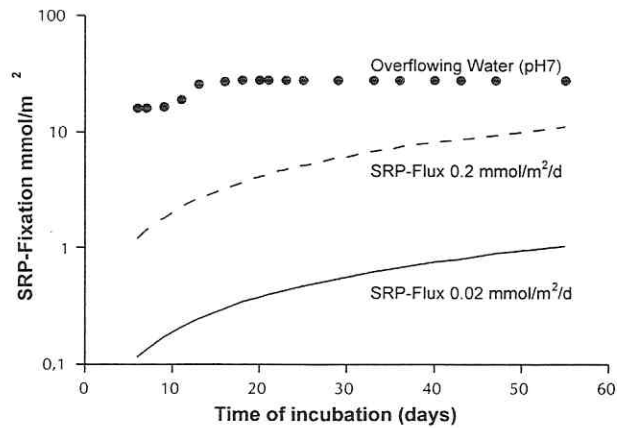


Fig. 8: SRP-fixation in the overflowing water of experiment 2 and potential SRP-fixation from two SRP-fluxes (according calculated SRP-fluxes of experiment 2 and 3 for pore water data after 8 weeks of incubation).

After 8 weeks, almost the entire SRP (< 0.009 mg/l) was removed from the overflowing water. However, the incubation experiments with the addition of P-enriched Fe(III) hydroxide sludge began with extremely high SRP pore water concentrations, which is not to be found in 'natural systems' (see Section 3.5).

In anoxic conditions in the overflowing water all cycles reveal an increase in SRP but not in Fe concentrations. In the sediments of Experiments 2 and 3 almost the entire pool of Fe and SRP were contained in iron phosphate (see Section 3.4), so that little SRP release through Fe(III) reduction could take place. This indicates that within this time period the SRP recently bound through the

sulphide formation in the sediments (demonstrated by Wendt-Potthoff and Langner, 2001) is not displaced (similarly found by Roden and Edmonds (1997). Here too, the high Fe concentrations

in the pore water play a decisive role. The model developed by von Hasler and Einsele (1948) and confirmed by Caraco et al. (1989, 1993) suggests that the availability of P and the Fe/P ratio in the anoxic bottom water is controlled by the sulphate concentration due to the iron sulphide formation (soluble Fe^{2+} from anoxic bottom water). This model cannot be applied here, since both the SO_4^{2-} and Fe concentrations in the pore water are much higher than in the bottom water and Fe is the available binding partner for the formation of H_2S which cannot be extracted from the bottom water. This is also confirmed by the SO_4^{2-} contents in the overflowing water (data not shown), which do not decrease during the demonstrated sulphide formation in the sediment but, independent of the incubation conditions, slightly increase.

P-Forms and Phosphates Equilibriums

According to Psenner et al. (1984), the P extractions at the sediments of the acid mining Lake Niemeck show that the particulate phosphorus in the sediment is dominated by BD and NaOH extractable P (Fig. 9). The largest portion consists of the BD fraction found in the sediment trap material before the flooding (11/98) and the upper 10 centimetres of the initial sediment. In the deeper layers the relationship to NaOH fraction changes. Since the SRP contents in the initial sediments closely corresponds to the TP contents in the extractions, the largest portion of P is inorganically bound (*sensu* Psenner et al., 1984). The high BD soluble P fractions are, according to Jensen and Thamdrup (1993), specific for iron-bound P in oxidized, amorphous and poorly crystalline iron species.

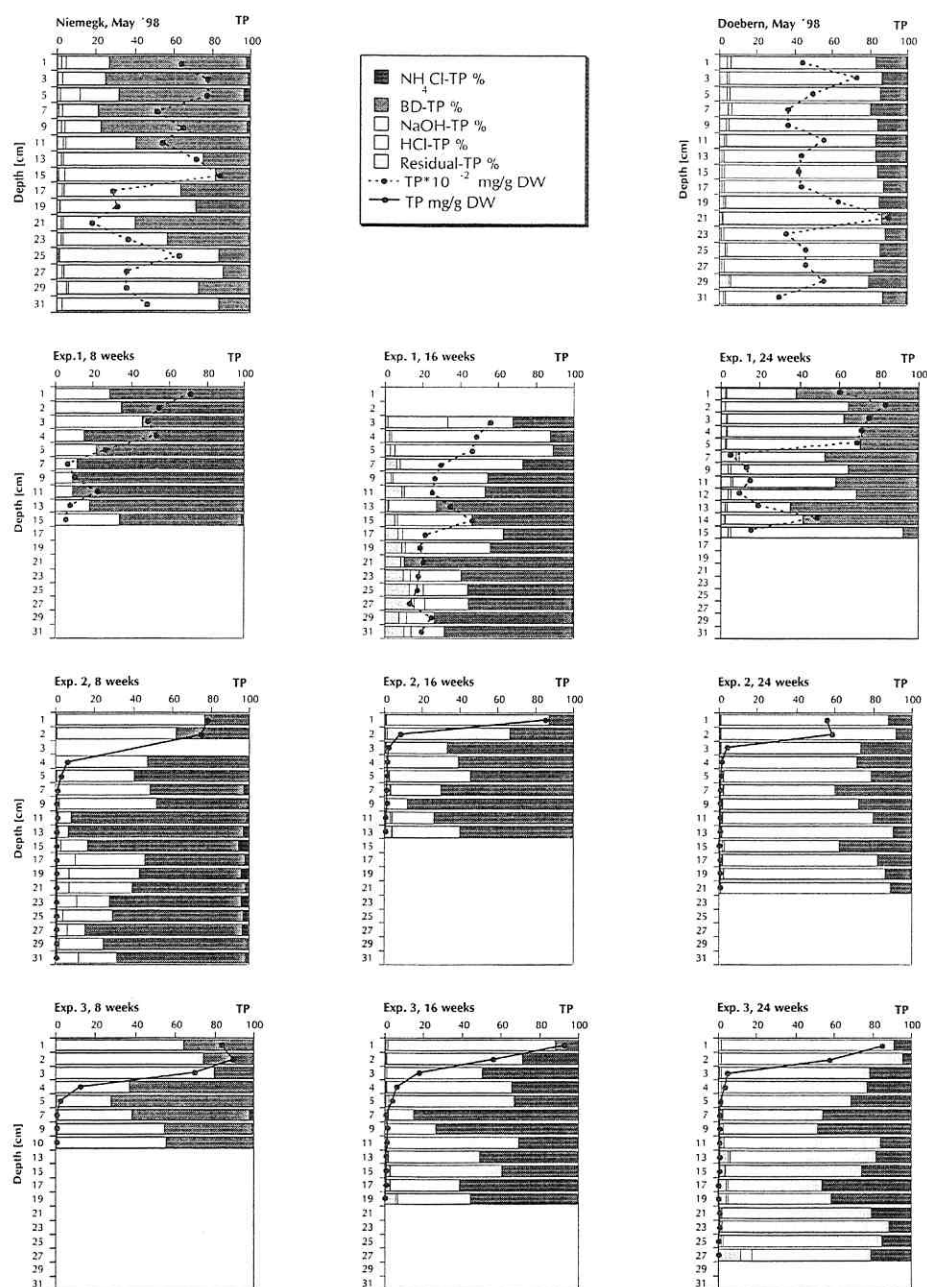


Fig. 9: TP-concentrations and extractions of the sediment in start (Lake Niemegek) and Lake Doebern and during the incubation.

This category includes the mineral schwertmannite, which is typical for the sediments of acid mining lakes (Bigham et al., 1996, 1990; Schwertmann et al., 1995), whose presence has been determined in many examined sediments (Langner et al., 2001). The extractions of the experimental sediments show that within 6 months all incubations were phosphorus enriched in the NaOH fraction. However, in Experiments 2 and 3, the layers near the surface and the layers deeper within the sediment must be differentiated.

The iron sludge, whose sediment surface was enriched with PO_4^{3-} , could be completely extracted with the BD solution at the beginning of the experiments. During the process of the incubations, the bonding relationship changed from P to NaOH-extractable P. Already after 8 weeks, 75% of the P fraction in the uppermost sediment layer with pH-neutral overflowing water could be retrieved in the NaOH extraction; 60% was retained with acidic overflowing water. In the underlying layer (1-2 cm depth), the relationship was reversed. From this it can be concluded that P conversion is promoted under pH neutral conditions. At the end of the experiments, 90 % of the P fractions were extractable with NaOH for both incubation procedures.

Since Wendt-Potthoff and Langner (2001) could determine high Fe(II) contents in the sediments, which after 8 weeks constituted more than half of the total easily available Fe, Fe(II) can become a binding partner for P in the form of vivianite. Geochemical equilibrium calculations with PHREEQC (Parkhurst, 1995) of the sediment pore water indicate that in the upper 2 to 3 centimetres the formation of vivianite is possible. Fig. 10 depicts a stability diagram of vivianite calculated with $\log K = -36.0$ (Nriagu, 1972) and $\log K = -33.5$ (Tessenow, 1974) as a function of the PO_4^{3-} concentration and the pH value. It becomes clear that with PO_4^{3-} a precipitation of this mineral is possible for contents already at pH values between 4.5 and 5. This geochemical environment is comparable with conditions in the uppermost centimetres of the sediments with

acidic overflowing water after 8 weeks. The calculations indicate that the contents in the pore water are determined by the geochemical equilibrium of vivianite. Hence, if the pH increases due to $\text{Fe}(\text{OH})_3$ dissolution, the P concentration decreases due to the vivianite precipitation. Thus, neutral conditions in overflowing water favour P fixation in the sediment and diminished pore water concentrations. Analyses, with the aid of Mößbauer spectroscopy, of the uppermost sediment layers of Experiments 2 and 3 led to the following two interpretation possibilities: (i) vivianite is almost the only Fe^{2+} containing phase, whereby 40-60 % of the Fe portions are present in the Fe^{3+} state; or (ii) a mixture of vivianite, FeS_2 , fine-grained FeS , FeCO_3 and $\text{Fe}(\text{III})$ oxides, or any combination thereof, is present.

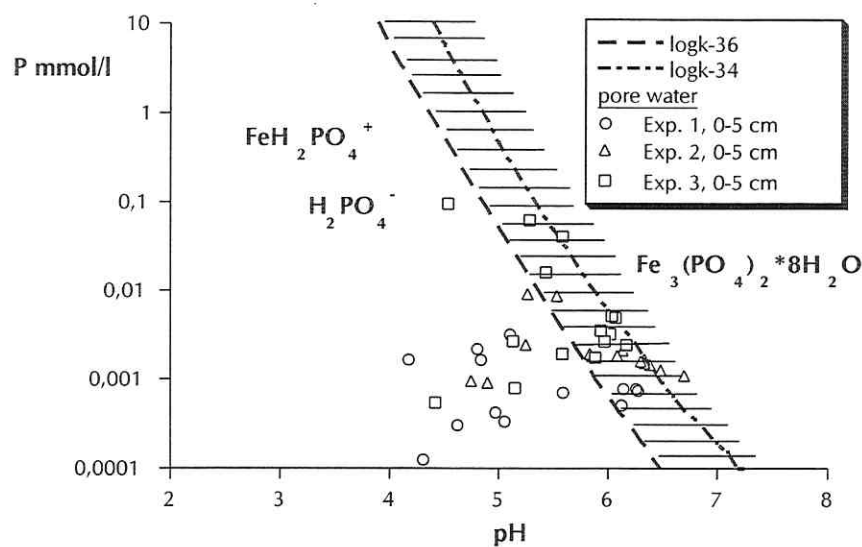


Fig. 10: Stability diagram of vivianite calculated with $\log K = -36.0$ (Nriagu, 1972) and $\log K = -33.5$ (Tessenow, 1974) as a function of the PO_4^{3-} and pH.

Since no carbonate was found and the maximum S contents constitute only 25 mg/g DW (data not shown), the Fe^{2+} containing phases (besides vivianite) could only form a small fraction of the total ferrous content. Additionally, extractions from Wendt-Potthoff and Langner (2001) showed that after 6 months incubation > 90 % of the entire bioavailable Fe is present as Fe^{2+} , so that the Fe(III) contents in oxide portions (initial $\text{Fe}(\text{OH})_3$ sludge) constitutes less than 10%. From this it can be concluded that vivianite can be the main phase in the upper layer of the sediments and, as similarly described by McCammon and Burns (1980) and König (1990), only by the preparation of the sample are the Fe fractions oxidized to vivianite. Thus, the NaOH soluble P fractions in the sediment close to the surface at the end of Experiments 2 and 3 reflect the substance conversion from $\text{Fe}(\text{OH})_3$ -adsorbed phosphorus to vivianite-bound phosphorus.

A different behaviour was evident of the sediments of Experiment 1 and the deeper sediment layers of Experiments 2 and 3, whose P portion after a 6 month incubation period could be detected in the NaOH fraction. This means, that the P bonds change independent of the different incubation conditions. It is possible that in the initial sediments the high P portions in the NaOH fractions can be found below a depth, where Fe-oxides due to the mineral transformation from schwertmannite to goethite were present in more crystalline form (Langner et al., 2001). Since the mineral transformation to goethite proceeds via a dissolution of the schwertmannite (sensu Biggam et al., 1996), the thereby released SRP can be precipitated as vivianite given the appropriate pH values. However, this is in conflict with the saturation indices of vivianite in the deeper sediment layers (calculated with PHREEQC, Parthurst, 1995). Additional bond formations would be crystalline Fe-hydroxide and goethite, which in the previous extraction step could possibly not be dissolved, since, as indicated above, the BD extraction is specific for amorphous and poorly crystalline Fe(III) oxides (sensu Jensen and Thampdrup (1993). The indirect binding

to goethite via the linkages of humic substances to phosphate represents an additional bond formation for P. The SRP released during the mineral transformation could be bound to the humic substances, which, according to Langner et al. (2001), originate as degraded products from the coal in deeper sediment layers which are dissolved by the NaOH extraction. The predominantly NaOH soluble phosphorus in the pH-neutral mining lake Doebern, whose mining residuals consist largely of goethite (see Fig. 9) (Langner et al., 2001), is also indicative of goethite-bound P portions in the NaOH extractions.

For the initial sediments and the sediments of the experiments, in which no Fe(III) reduction was determined, the question remains as to what P-bond formation dissolved in the NaOH extraction is found in the sediments. The development of the TP contents in the sediments during the incubations shows that no substantial change in location in the phosphorus takes place. After 6 months incubation, almost the entire portion of the P amount was retrieved in the solid phase, which leads to the conclusion that the P fixation rate must have been very high. Vivianite must have formed within a layer only a few centimetres thick where the conversion of $\text{Fe}(\text{OH})_3$ took place.

Expected Trend of P-Retention in flooded Mining Lakes

The TP content of 0.2-0.9 mg/g DW in the Lake Niemegek sediments is similar to that found in other mining lakes flooded with ground water (Friese et al., 1998). The contents of < 1mg/g DW are, in comparison with sediments of natural lakes, rather low (Hupfer, 1996). The P sedimentation in mining lake Niemegek during the flooding was calculated from the sediment trap material (6/99, 11/99, 4/00) to be $3 - 4 \text{ g m}^{-2} \text{ a}^{-1}$, which is three times lower than the P sedimentation found in the acid mining lake Golpa, which is also being flooded with water from

the river Mulde (Hupfer et al., 1998).

In order to draw conclusions for the P retention in acid mining lakes that are being flooded or have already been flooded, it is important to transfer the results from the incubation experiments to the conditions found in the lakes. Predictions indicate that during the flooding, a large part of the phosphorus from the river water is adsorbed to and sedimented by the iron hydroxides in the lake (Limnological Expertise assessment, 1994). This is supported by investigations with sediment trap material collected in the mining lakes Muehlbeck and Niemegek during their flooding. Up to 43 % of the sedimented phosphorus was found in the BD fraction (data not shown). The phosphorus released during the Fe(III) reduction can be precipitated in the sediments as vivianite (re-precipitate), according to results of the incubation experiments. How high the P flux will be in the bottom water depends largely on the conversion and precipitation rates in the sediment, which are determined by the geochemical conditions (especially the pH).

On the one hand it is important to estimate how large the Fe(III) reductions are, since they, too, control the P release and pH value in these sediments. Investigations by Wendt-Potthoff and Langner (2001) show that, with the presence of a carbon source, almost the entire portion of Fe(III) is reduced to Fe(OH)₃ within 16 weeks. Here the surrounding conditions in the overflowing bottom water play only a subordinate role. pH conditions had more influence on the conversion location, which was found in the bottom water 1 cm deeper in the sediment with acidic conditions. Taking an average value of 250 mg Fe/g DW in the sediment, a Fe/P atomic ratio of 60-150 is calculated. Since the Fe/P ratio is very high compared to other eutrophic lakes (Baccini, 1985, Hupfer et al., 1998), the SRP release from the dissolution of iron hydroxide will be substantially smaller, even with high Fe(III) reduction rates. With the maximum Fe(III) reduction rates of $3.5 \mu\text{mol cm}^{-3} \text{ d}^{-1}$ derived from the incubation experiments, a SRP 'gross

release' of $23\text{--}58 \text{ nmol cm}^{-3} \text{ d}^{-1}$ was predicted for these future lake sediments (under the condition that all the P is bound to Fe). This corresponds to approximately $230\text{--}580 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$ in a reduction zone of 1 cm thickness.

The SRP content released during the Fe(III) reduction is reduced by adsorption and precipitation processes in the sediment. Hence, the SRP portion available for transport into the bottom water is much smaller, reflected in the smaller pore water concentrations. The retention capacity of the sediments, which according to Baccini (1985) can be expressed by the Fe/P atomic ratio in the pore water of the reduction zone, is particularly important for the P flux from the lake sediments into the bottom water. The larger the ratio, the smaller the P flux is from the sediment to the water. However, the investigations (Lean et al., 1986; Baccini, 1985) were all carried out in pH-neutral conditions and never in conditions comparable to the geochemical environment.

From the literature it is well known that P competes with H_2S for Fe as a potential binding partner (Roden and Edmonds, 1997; Kleeberg and Kozerski, 1997), hence the Fe concentrations in the pore water are of crucial importance. Since the Fe contents of 1–4 g/l in the pore water of the acid mining lakes are very high, no Fe limitation seems to be present in the examined sediment systems at the initial stages. The incubation experiments show that the Fe conversion and fixation rates are much higher than the formation of sulphide as long as iron phosphate is available. However, the incubation period of 6 months is too short to predict the long-term behaviour of the sediments, since the displacement of P by sulphide is a diagenetically long-term process. The sediments, which consist almost exclusively of iron hydroxides, function both as an Fe source, as well as a potential adsorbent pool for phosphorus. The specialty of this system exists predominantly in acidic conditions, which play a key role in the re-precipitation of P (see Section 3.4). Fig.11 depicts the factors that influence the pH value in the sediment and the

resulting SRP concentrations in the pore water.

According to Langner et al. (2001), the pH values in these mining lakes are particularly determined by the following processes: (i) Fe(III) reduction (increases pH), (ii) mineral transformation of schwertmannite to goethite (decreases pH), and (iii) high diffusive addition of H^+ from the bottom water (decreases pH). As indicated by the geochemical modelling of the initial sediments (Langner et al., 2001), the H^+ flux from that overflowing water in the upper sediment layer appears to have a dominant effect. It is controlled by the pH value attained in the sediment, the SRP concentrations in the pore water and the resulting flux due to geochemical equilibrium conditions. With the latter, the distance between the reduction zone and the sediment surface is of crucial importance.

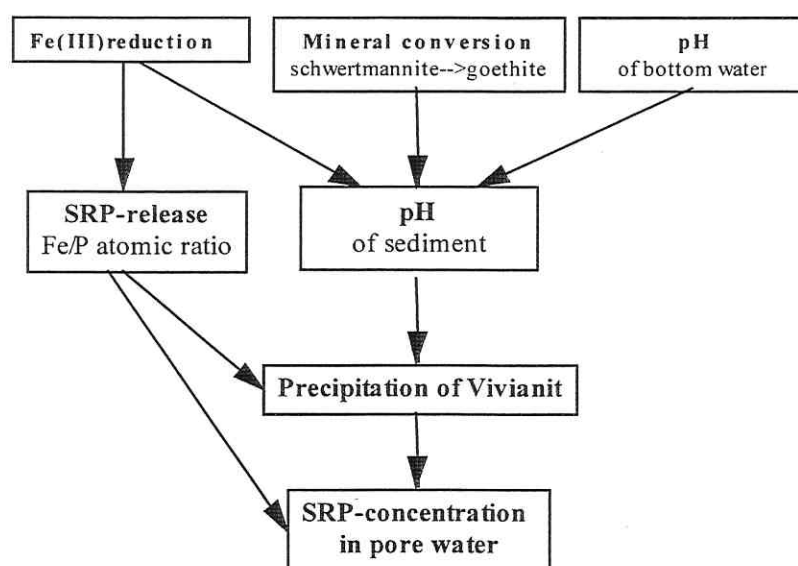


Fig. 11: Scheme of factors that influence SRP-concentrations in pore water.

A high portion of the Fe-hydroxides is expected to consist of a large fraction of goethite since, according to initial investigations, the precipitation of the Fe-hydroxide occurred at the boundary layer between supplied river water and lake water under less acidic conditions ($\text{pH} > 3.5$). Thus, a large fraction of P is bound to more poorly available Fe-hydroxide (for microbial activity), of which less can be released.

Just as the geochemical conditions in the sediment strongly change during and after the flooding of the acid mining lake, so, too, will the SRP flux into the bottom water vary temporally. Fig. 12 depicts the SRP fluxes for the upper sediment layer (0-1 cm), which were calculated using different assumptions in the initial concentrations of SRP in the pore water, the 'net release rate' of SRP in the sediment and the SRP concentrations in the bottom water (according to incubation experiments after 8 weeks).

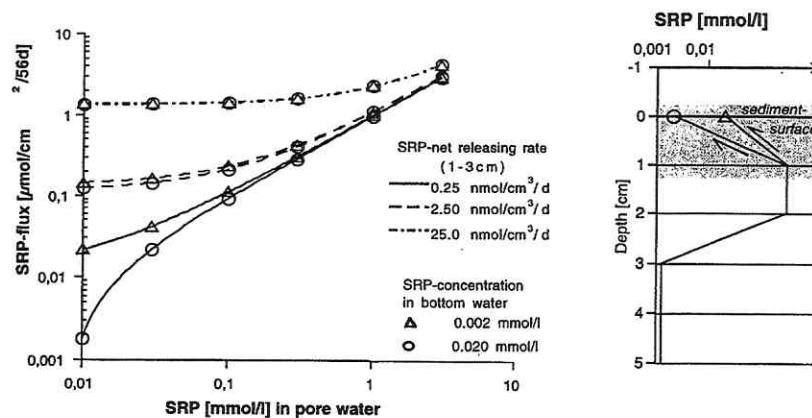


Fig. 12: Calculated SRP-Fluxes of the upper sediment layer for different pore water and bottom water concentrations depended of SRP-net releasing rates in the sediment (1-3cm).

After 8 weeks, SRP 'net release rates' ranging between 2.5 and 25 nmol cm⁻³ d⁻¹ were calculated from the sediments in the incubation experiments with pH-neutral and acidic overflowing water. This corresponds to 50-500 μmol m⁻² d⁻¹ with a reduction zone of 2 centimetres. However, due to the extremely high SRP supply through the addition of P, which is not expected to occur in lakes, the SRP fluxes in the upper layer of the incubation sediments represent maximum values. Since the SRP concentrations in the pore water will increase more slowly than in the incubation experiments, due to the low release rates (high Fe/P), the thermodynamic equilibrium of vivianite is expected to be reached only with higher pH values (> 5.5). Hence, the SRP concentrations in the pore water of the reduction zone of the future lake sediments and the resulting SRP fluxes will be smaller than those found in the incubation sediments with pH-neutral overflowing water.

CONCLUSION

Incubation experiments on sediments from acid mining lakes show that within 16 weeks almost all of the phosphate adsorbed to Fe(OH)³ is completely converted to vivianite, if an ample supply of carbon is available. The surrounding conditions (pH, O₂ content) in the bottom water do not have a strong influence on the magnitude of the Fe(III) reduction and hence, also do not strongly effect the phosphate release in the sediment. The conversion of dissolved phosphate to vivianite is, however, controlled substantially by the pH development in the sediments. According to Langner et al. (2001), the pH conditions in these acid mining lake sediments are dominated by the Fe(III) reduction, the mineral transformations from schwertmannite to goethite and the influence of the pH conditions in the bottom water.

The thermodynamic equilibrium of vivianite seems to control the SRP concentrations in the pore water. If the bottom water is acidic (pH = 3), the SRP concentrations in the uppermost sediment layer (0-1 cm) adjust to a value of 100 mmol/l, which is an order of magnitude higher than with pH-neutral bottom water. The highest SRP fluxes into the overflowing water, which were calculated from the SRP gradients in the pore water, were approximately $0.2 \text{ mmol m}^{-2} \text{ d}^{-1}$ for acidic overflowing water (pH = 3) and $0.02 \text{ mmol m}^{-2} \text{ d}^{-1}$ for pH-neutral overflowing water after 6 weeks incubation.

The binding behaviour of P changes in the deeper sediment layers, which becomes evident by the rise of the NaOH-soluble P fractions. This is probably caused by the mineral transformation from schwertmannite to goethite, which, according to Bigham et al. (1996), is carried out by the dissolution of schwertmannite. In the process, the sorbed P portion can be released to form new bonds. The formation of sulphide does not negatively affect the P concentration in the bottom water (in an anoxic state for 4 weeks), since the Fe concentrations in the pore water are very high and the Fe is available as binding partner for P.

If one transfers the incubation experiments over to the flooding scenarios of the mining lakes, a smaller SRP flux is expected to be found in the mining lakes than in other eutrophic lakes even under seasonal anaerobic conditions (Moore et al., 1991; Baccini, 1985; Emerson and Widmer, 1978). This is particularly promoted by a rapid pH rise in the bottom water, which can be influenced substantially by the flow rate. The high Fe/P atomic ratios both in the fixed phases and in the pore waters of the sediments support the smaller SRP flux into the bottom water. An iron limitation, which is under much discussion in the literature (Kleeberg and Kozerski, 1997; Hupfer et al. 1998; Emerson and Widmer, 1978), is not expected to occur in these sediment systems. The iron fractions guarantee a high fixation rate of the dissolved SRP as vivianite and a sorptive bond

to iron hydroxides. Since, with rising pH values, the iron hydroxide pool in the sediments turn into more crystalline forms such as goethite (Langner et al., 2001) (which according to Lovely and Phillips (1986) is, from a microbial perspective, poorly available)), only small Fe(III) reductions and their resulting SRP releases in deeper sediment layers are expected to be found. This will hardly influence the SRP fluxes into the water column.

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2.3

Biogeochemical changes in acidic lignite mining lake sediment after organic carbon and phosphorus supplementation

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Abstract - One strategy to remediate acidic mining lakes is flooding of the mine pit with river water. The different possible effects of flooding on the lake sediment were simulated in a mesocosm experiment using intact sediment cores. Plankton material and Fe hydroxides enriched with phosphorus were applied to the sediment surface to mimic the expected Fe precipitation and organic carbon supply by plankton sedimentation. The overflowing river water was kept acidic or neutral to simulate different stages of the flooding process. Additions stimulated microbial activity and proliferation whereas neutral water alone had little effect. A reducing zone with elevated pH was generated near the surface where Fe(III) reduction and sulfate reduction subsequently occurred. In the first period accumulation of Fe(II) phases was observed in this zone and later sulfide phases were formed. Fe(II) oxidation was inhibited in this zone, but recovered to initial values after prolonged incubation of the assays. Bacterial numbers generally followed the observed activities. Our results show that easily degradable organic matter is crucial for microbial alkalinity generation and water pH is of minor importance. As a consequence, the use of a nutrient-rich productive river for mine pit flooding is expected to have beneficial effects on the water quality of the treated lake.

INTRODUCTION

Lakes resulting from opencast lignite mining are often affected by severe acidification (pH values typically between 2.3 and 3) due to oxidation of sulfide minerals in the overburden material (Nordstrom 1982). As a result of the acidity, they possess high Fe and sulfate concentrations, extremely low carbon content, low productivity and a very restricted biocoenosis consisting of few tolerant species (Deneke 2000, Lessmann et al. 2000, Packroff 2000, Wollmann et al. 2000). If left untreated, these extreme conditions persist for decades or even longer, as can be seen in the older mining lakes in the Lusatian district (Lessmann et al. 1999).

There are several strategies for abatement of acidification, for reviews see Wendt-Potthoff and Neu (1998) or Schultze et al. (1999). Liming is not feasible because the strong acidity produced by the iron buffer would demand orders of magnitude higher additions than those used for lakes acidified by atmospheric deposition. Moreover, the neutralization would not be sustainable if the lake receives acidic inflows by groundwater or surface water. Addition of organic substrates to stimulate microbial iron and sulfate reduction seems promising, especially for smaller lakes, although no full scale treatment method for whole lakes is available in practice yet. Flooding of the mine pit with river water before it fills by ascending groundwater is the method of choice, if a river with sufficient water of good quality is available. This is a prerequisite, since nutrients and contaminants carried by the river water will accumulate in the lake.

In the case of lake Niemegk (near Bitterfeld, Germany) flooding with river Mulde water began in 1999. Expected initial effects of this treatment were Fe(III) precipitation due to the shift in pH, sedimentation of plankton not viable at pH 3, and after several years, neutralization of the water column (Limnological expertise). The sedimentation of plankton material also results in organic carbon supply to the sediment.

Previous studies on remediation of acidic waters focused on development of water quality (e.g. Christensen et al. 1996, Fyson et al. 1998). The aim of this study was to simulate these different effects of flooding with river water on the biogeochemistry and microbiology of the lake sediment under controlled laboratory conditions before the actual flooding started. Three different geochemical situations were compared with respect to their effects on microbial population dynamics and activities, with special focus on the microbial Fe cycle.

MATERIALS AND METHODS

Study site

Mining Lake Niemegk was a small mining lake in the abandoned lignite mine Goitsche near Bitterfeld, Germany. Today it is a subbasin of the Goitsche mining lake (Schultze et al., submitted). A detailed description of the geochemical characteristics of Lake Niemegk can be found in Langner et al. (submitted). In May 1998, 10 apparently undisturbed sediment cores were obtained by gravity coring. One core was immediately sampled to determine starting conditions, the other 9 cores were directly used as mesocosms in the laboratory incubation experiment.

Experimental design and sampling

The sediment incubation system has been described in Langner and Friese (submitted). Briefly, intact sediment cores were incubated in the dark for 24 weeks with temperature set at 10°C. Three cycles, each with three sediment cores, were run in parallel. River Mulde water was continuously circulated from a reservoir over the sediment surfaces. Water in the reservoirs was replaced after

each sediment sampling. The pH value of the overflowing water was regulated using a feedback controlled simulation unit (Langner and Friese, submitted).

In a first treatment (Exp. 1), the sediment was overflowed with neutral river water without further supplements. The second treatment (Exp. 2) received the same water and in addition, plankton biomass from a reservoir flown through by River Mulde and phosphorus-enriched Fe hydroxide were placed on the sediment surface. The added material consisted of 80 ml of a FeOH_3 slurry (344 mg g-dw^{-1}) with adsorbed phosphate prepared according to Lovley and Phillips (1986a) and 15 ml of plankton material simulating a POC sedimentation of $750 \text{ mg m}^{-2} \text{ d}^{-1}$ for the first 8 weeks. After 8 and 16 weeks, additional plankton material corresponding to a POC sedimentation rate of $450 \text{ mg m}^{-2} \text{ d}^{-1}$ was supplied to the remaining cores. The third treatment (Exp. 3) received plankton biomass and P-enriched Fe hydroxide in the same way, but the overflowing river water was acidified to pH 3.

Every 8 weeks, one core of each cycle was removed and sliced cm-wise in a glove box filled with N_2 . Cores were sectioned in slices of 1 cm (0-10 cm depth) or 2 cm (10-20 cm depth) and transferred into 50 ml polyethylene centrifuge tubes (during this process the upper 2 cm of the 16 weeks core of Exp. 1 were lost so that data from these samples are missing). Samples were homogenized, and pH and E_H values were measured with electrodes (SENTIX-41, SENTIX-ORP, WTW). Subsamples for extraction of iron bonded forms and for microbiological investigations were filled into centrifuge tubes and into sterile brown glass vials. In addition we filled 2 ml microtubes for determination of water content and porosity. Tubes for pore water collection were centrifuged at 3800 rpm for 10 minutes and returned to a glove bag where pore water was collected into plastic syringes and filtered through $0.45 \mu\text{m}$ cellulose acetate filters. Before use the filters were washed with 60°C hot distilled water in order to minimize background DOC

concentrations. Pore water samples were diluted with HCl-acid water (pH 2) for chemical analyses. The solid phases were immediately frozen at -40°C and freeze-dried under vacuum.

Chemical analyses

Total Fe in porewaters was determined by ICP-OES. Fe^{2+} was determined with a spectrophotometer (DU-600, BECKMAN) using Ferrozine according to Stookey (1970). DOC concentrations were obtained using a Carbon-Analyzer (DIMATOC-100, DIMATEC). SO_4^{2-} was analyzed with a ion-chromatograph (ICA-5000, GAT). HCl-soluble Fe(II) and hydroxylamine-reducible Fe(III) in wet sediment were determined in triplicates according to Lovley and Phillips (1987). Samples were centrifuged ($16.000 \times g$, 10 min) instead of filtration before photometry.

Acid Volatile Sulfide (AVS: FeS) and Chromium Reducible Sulfide (CRS: FeS + FeS₂) were extracted from freeze-dried sediment subsamples. The distillation procedure was adapted from Haese et al. (1997), Fossing and Jørgensen (1989) and Canfield et al. (1986). Samples were distilled at room temperature to avoid extraction of S⁰. H₂S was swept by carrier gas into a trap with SAOB (Sulfur Antioxidant Buffer) solution (Cornwell and Morse 1987). Sulfide concentrations were determined by polarography (MDE-150, RADIOMETER, Inc).

Microbiological analyses

Bacterial populations and activities were determined in the upper 20 cm of the sediment or in all layers if the core was shorter. Potential activity of Fe(III) reducing bacteria was assayed using synthetic amorphous Fe oxyhydroxide. It was synthesized and washed according to Lovley and

Phillips (1986b), dispensed to brown glass vials, purged with N_2 and autoclaved. Five ml of synthetic Fe oxyhydroxide slurry were combined with 1 ml of wet sediment in an anoxic chamber (95:5 $N_2:H_2$ atmosphere), mixed and analyzed for HCl-soluble Fe(II). Duplicates poisoned with $HgCl_2$ were prepared from some samples to check for possible abiotic Fe(III) reduction. After 6 days incubation at 20°C in the dark, accumulation of Fe(II) was determined for the second time. A third measurement was taken after 13 or 14 days. Unfortunately the assays from May 1998 (starting conditions) seemed to be oxidized after the second sampling, as shown by a decrease in Fe(II) concentration in all vials. Therefore only two measurements were used for rate calculation from this core.

Potential Fe(II) oxidation was determined in a Fe(II)sulfate medium (KH_2PO_4 0.8 g, $MgSO_4 \cdot 7H_2O$ 0.8 g, $(NH_4)_2SO_4$ 0.8 g, $FeSO_4 \cdot 7H_2O$ 66.6 g, 0.1 N H_2SO_4 1000 ml, pH 1.4 adjusted with H_2SO_4), mixed with an equal volume of 0.2 μm filtered reservoir water. 20 ml of this solution were filled into 50 ml tissue culture bottles. Before and after addition of ca. 0.5 ml sediment the bottles were weighed. Incubation was performed at 20°C in the dark without shaking but in horizontal position to ensure oxygen supply. In intervals of a few days the bottles were sampled for Fe(II) analysis. Duplicates poisoned with $HgCl_2$ from some samples served as abiotic controls. The latest three time points of the Fe(II) measurements were used to calculate Fe(II) oxidation rates per g wet sediment. By this the influence of an initial lag phase on potential Fe(II) oxidation was minimized.

Bacterial populations were enumerated by dilution culture series (Most Probable Number, MPN). The compounds of the basal mineral medium for iron-oxidizing bacteria (FeOB), sulfur-oxidizing bacteria (SOB) and sulfate-reducing bacteria (SRB) were (in $g\ l^{-1}$) 0.1 KH_2PO_4 , 0.1 NH_4Cl , 0.1 $NaCl$, 0.1 KCl , 0.2 $CaCl_2 \cdot 2H_2O$ and 0.2 $MgCl_2 \cdot 6H_2O$ and 1 ml l^{-1} trace element solution SL12B

(Widdel and Pfennig 1981). Additions for FeOB were $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (80 mM) and Vitamin B_{12} ($40 \mu\text{g l}^{-1}$). Additions for SOB were $\text{Na}_2\text{S}_2\text{O}_3$ (10 mM), Vitamin B_{12} ($40 \mu\text{g l}^{-1}$) and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (1 mg l^{-1}). The medium was phosphate buffered ($6.7 \text{ mM KH}_2\text{PO}_4$) and posed to pH 4.5. Bromophenolblue (5 mg l^{-1}) was used as pH indicator. Additions for SRB were $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (15 mM), selenite-tungstate-solution ($1.2 \mu\text{g l}^{-1} \text{Na}_2\text{SeO}_3 \cdot 5\text{H}_2\text{O}$ and $1.6 \mu\text{g l}^{-1} \text{Na}_2\text{WO}_4 \cdot 5\text{H}_2\text{O}$, Widdel and Bak 1992), vitamin solution (Stams et al. 1983, 1 ml l^{-1}), sodium lactate (5 mM), sodium acetate (5 mM) and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (0.05 g l^{-1}). The medium was carbonate buffered (20 mM NaHCO_3) and poised to pH 7. The medium for Fe(III) reducing bacteria (FeRB) was adapted from a medium for *Geobacter metallireducens* (DSM no. 579). It contained (in g l^{-1}) 13.7 ferric citrate, 1.5 NH_4Cl , 0.6 NaH_2PO_4 , 0.1 KCl , 1.6 sodium acetate, 0.05 yeast extract, $0.25 \text{ mg l}^{-1} \text{Na}_2\text{WO}_4 \cdot \text{H}_2\text{O}$ and 10 ml l^{-1} trace elements solution (Lovley et al. 1984). The medium was buffered with 10 mM MES (2-morpholinoethanesulfonic acid) and poised at pH 6. SRB and FeRB media were cooled under N_2 after autoclaving. Dithionite was used as reducing agent for the SRB medium. All MPN cultures were prepared in deep multiwell plates (8 parallels) and incubated at 28°C in the dark for 6 weeks. Anoxic conditions for anaerobes were generated by placing cultures in sealed bags with gas generators (Merck Anaerocult A). Indicators for growth were formation of orange or brown precipitates for FeOB, colour change from blue to yellow for SOB and black precipitates for SRB. Growth of FeRB was judged from accumulation of Fe(II) determined in a microtiter format ferrozine assay. MPN were calculated with the program of Klee (1993).

The phospholipid phosphate content was determined from duplicate subsamples as an estimate of total viable microbial biomass. The method of Frostegard et al. (1991) was applied with the modifications suggested by Neumann (Ph.D. thesis, University of Marburg, 1995). To provide

comparison with culturable bacterial populations, lipid phosphate concentrations were converted to cells ml⁻¹ using sediment bulk density and the conversion factors from Balkwill et al. (1988) as referenced in Tunlid et al. (1992).

RESULTS

Geochemistry

Profiles of pH (Figure 1) and inversely correlated E_H (Figure 2) show different trends in the three experiments. Whereas distinct peaks (up to pH 6) in near-surface layers of Exp. 3 indicate the development of a zone where alkalinity was generated, the profiles of Exp. 1 and 2 show non-stationary conditions. However, a clear increase in pH near the surface was also evident in Exp. 2. E_H values in the upper 3 cm of the sediment cores continuously decreased in all experiments (Figure 2) with the lowest values after 8, 16 and 24 weeks incubation in Exp. 2 (E_H: Exp. 2 < Exp. 3 < Exp. 1).

Similar to pH profiles the DOC concentrations in Exp. 3 showed small but stable peaks near the surface during the whole incubation (Figure 3). Discontinuous peaks in the other experiments indicate non-stationary conditions with respect to DOC.

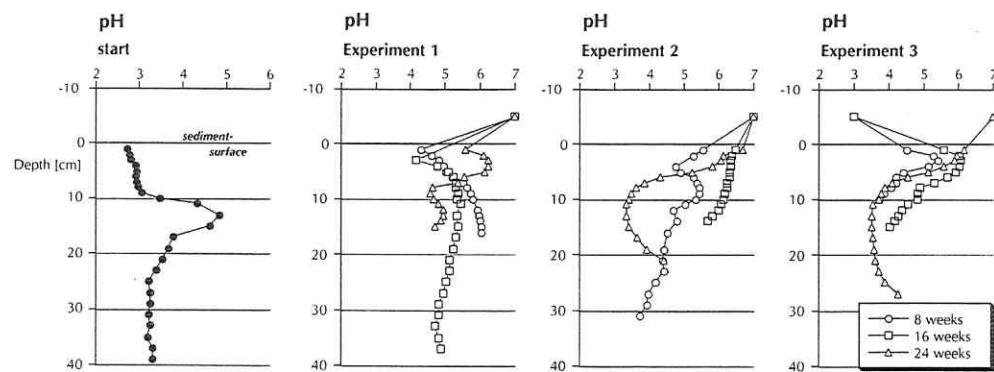


Fig. 1: Development of pH values with time in the 3 experiments.

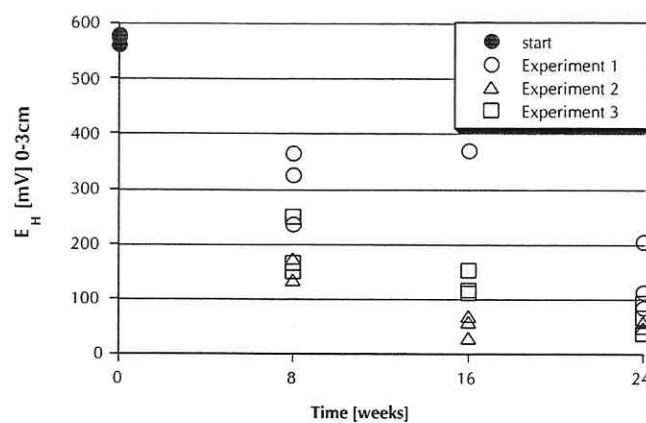


Fig. 2: Development of E_H values with time in the upper 3 cm in the 3 experiments.

The profiles slightly corresponded in shape with total viable biomass, but the relation was not quantitative since DOC sometimes had extreme values. An evident correlation with either pH or Fe(III) reduction activity did not exist. Interestingly, the two cores with extremely high DOC

concentrations (Exp. 1 after 8 weeks up to 100 mmol l^{-1} , Exp. 2 after 16 weeks up to 35 mmol l^{-1}) showed highly scattered Fe(III) reduction rates with often negative values.

The distribution of highly concentrated Fe and SO_4^{2-} in porewaters (up to 55 and 70 mmol l^{-1} respectively) did not show significant changes during incubation in any of the experiments (see Figure 3 as an example). Like at the beginning Fe and SO_4^{2-} were tightly correlated, but during incubation steepest concentration gradients developed in the upper centimeters, resulting in constant fluxes to the overflowing water.

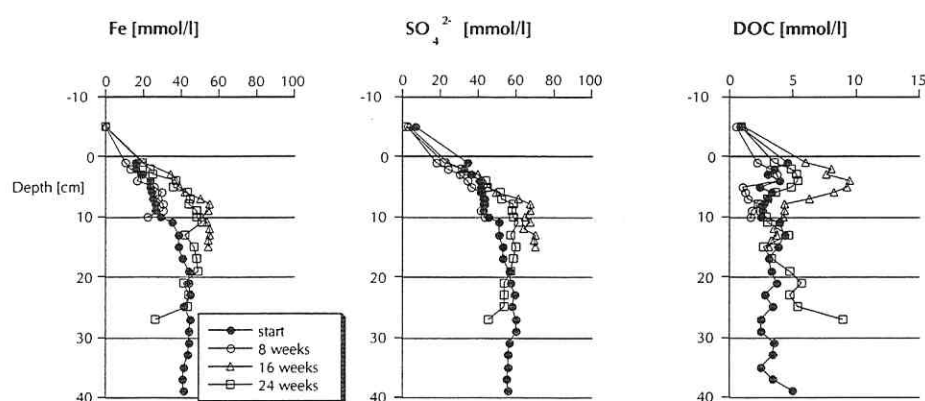


Fig. 3: DOC, total Fe and sulfate in porewaters of Exp. 3.

Total reactive (HCl-soluble + hydroxylamine-reducible) Fe per g wet weight was very high in Lake Niemegek sediment ($125\text{--}450 \mu\text{mol g-ww}^{-1}$, Langner et al. 2001) with elevated Fe(II) concentrations below 10 cm depth at the beginning of the experiment. However, most of the reactive Fe was Fe(III). HCl-soluble Fe(II) corresponded with concentrations in pore waters. In Exp. 2 and 3, HCl-soluble Fe(II) accumulated in the upper 2 cm after 8 weeks and hydroxylamine-reducible Fe(III) was almost depleted after 16 weeks. Fe(II) in porewater showed

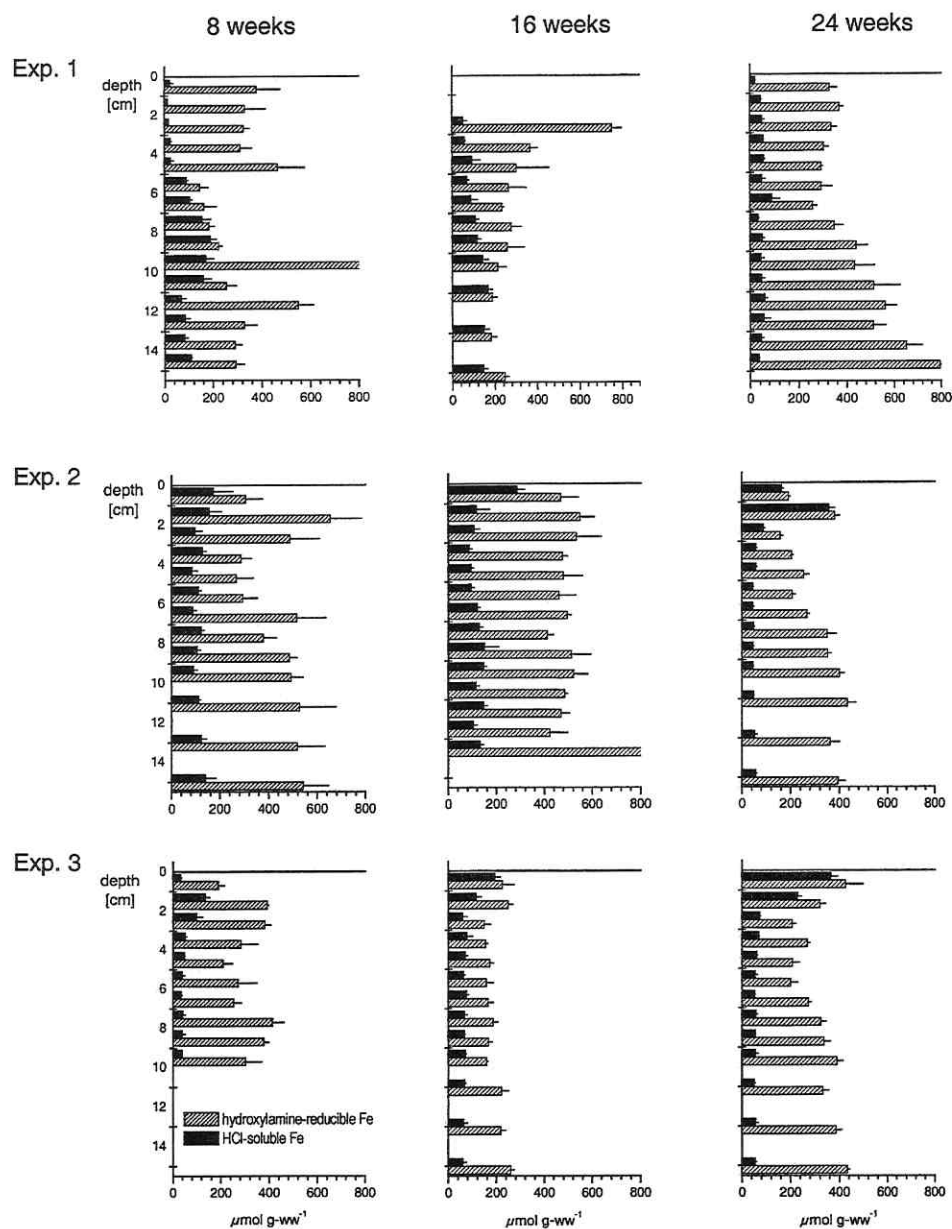


Fig. 4: Profiles of HCl-soluble and hydroxylamine-reducible Fe (FeII + FeIII). Error bars represent standard deviations from 3 replicates. Values below 15 cm were omitted since no further changes were observed.

an opposite trend in these cores with concentrations generally increasing with depth (Langner and Friese, submitted).

However, dissolved Fe(II) was only 20% or less of total Fe(II) in surface layers. In Exp. 1, most of the reactive Fe remained Fe(III) (Figure 4). Elevated concentrations of Fe(II) were found in deeper layers (5-11 cm after 8 weeks, >9 cm after 16 weeks, 6-7 cm after 24 weeks).

Reduced inorganic sulfides were initially present in very low concentrations. The CRS fraction representing $\text{FeS}_2 + \text{FeS}$ was below 1 mg g-dw^{-1} , (Table 1), and AVS was not detectable. In Exp. 2 and 3, accumulation of reduced sulfides was evident after 16 weeks and proceeded until 24 weeks to concentrations $>10 \text{ mg g-dw}^{-1}$ (Table 1). This gives clear evidence of microbial sulfate reduction in a later stage of the experiments. In Exp. 1, only after 16 weeks elevated concentrations of sulfides were detected at 2-3 and 10-11 cm which were not confirmed by extractions performed after 24 weeks. This core sampled after 16 weeks had a different mineral composition (Langner and Friese, submitted) and was therefore regarded as an outlier.

Table 1: Accumulation of reduced inorganic sulfides (AVS + CRS) in selected sediment layers.

✦ Experiment 1, ■ Experiment 2, ● Experiment 3. Number of symbols represents concentrations: ● = 1 mg/g dw, ●● = 10 mg/g dw and ●●● = 100 mg/g dw. N.d. not determined.

Depth [cm]	start	8 weeks	16 weeks	24 weeks
0-1	✦ ■ ●	✦ ■ ●	n.d. ■ ●●	✦ ■ ●●●
1-2	✦ ■ ●	✦ ■ ●●	✦ ■ ●●	✦ ■ ●●
3-4	n.d. n.d. n.d.	n.d. n.d. ●	n.d. n.d. ●	n.d. ■ n.d.
6-7 or deeper	✦ ■ ●	✦ ■ n.d.	✦ ■ n.d.	✦ n.d. ●

Biomass and cell numbers

Microbial biomass in Lake Niemegek sediment estimated from phospholipid P content initially showed two maxima with concentrations $>100 \text{ nmol g-dw}^{-1}$ near the sediment surface and between 12 and 20 cm depth, demonstrating that the lower Fe(III) reduction zone was a site of general microbial proliferation. The phospholipid P contents found before the experiments ($14\text{--}142 \text{ nmol g-dw}^{-1}$) are within the range determined for pristine sediments or freshwater streams (Dobbs and Findlay 1993). Assuming a relation of $100 \text{ } \mu\text{mol P g}^{-1} \text{ carbon}$, which applies for various bacteria (Dobbs and Findlay 1993), this results in $0.14\text{--}1.42 \text{ mg bacterial C g-dw}^{-1}$. However, reliable conversion factors for mining lake microbiota are still to be determined.

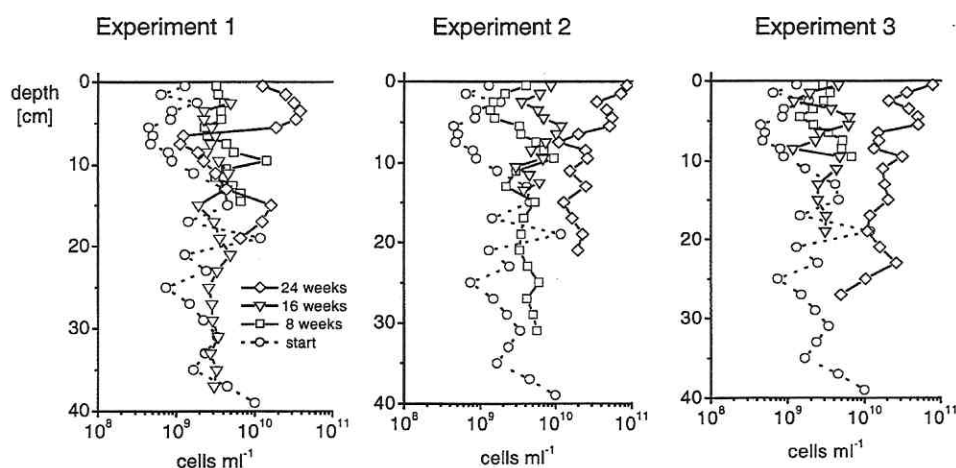


Fig. 5: Total viable bacterial cells per ml sediment as estimated from phospholipid phosphate extractions. Details see text.

Conversion to cells ml⁻¹ revealed an increase in bacterial abundance by 1-2 orders of magnitude after 24 weeks in all experiments (Figure 5). Exp. 2 and 3 developed a maximum in the upper 1-2 cm of the sediment where microbial biomass per g-dw was roughly doubled, corresponding to $\geq 10^{11}$ cells ml⁻¹. The second maximum broadened and moved upwards from around 10 cm depth after 8 weeks to 5 cm after 24 weeks. In Exp. 1 a bacterial maximum developed at 4 cm depth, but not at the surface. Culturable populations of iron and sulfur bacteria are displayed in Figure 6. Initially anaerobes (FeRB and SRB) occurred in very low numbers in the upper 10 cm of the sediment (10^2 cells ml⁻¹ or less).

Whereas SRB numbers were only slightly elevated between 10 and 20 cm, FeRB showed a pronounced maximum which could not be accurately resolved due to insufficient dilution. In contrast, FeOB and SOB numbers were high ($>10^6$ cells ml⁻¹) in the upper 12 cm. Due to insufficient dilution the FeOB maxima at 3-5 and 6-8 cm could not be exactly determined. Below

a minimum at 12-14 cm depth, which corresponds to the FeRB maximum, numbers increased again to around 10^6 ml^{-1} .

During sediment incubation, bacterial populations changed in different ways. FeOB and SOB showed an overall decline to 10^4 - $10^6 \text{ cells ml}^{-1}$ after 8 weeks and then remained fairly constant in all treatments. No distinct peaks were observed except a constant FeOB minimum in the upper cm of Exp. 2.

FeRB and SRB behaved differently in the three treatments. During Exp. 2, FeRB developed a gradient with highest numbers around 10^5 ml^{-1} near the sediment surface. SRB proliferated faster and more intense, especially in the upper 4 cm where a surface maximum of $>10^6 \text{ ml}^{-1}$ had developed after 16 weeks which persisted until 24 weeks. Development of FeRB and SRB populations in Exp. 3 was similar to Exp. 2.

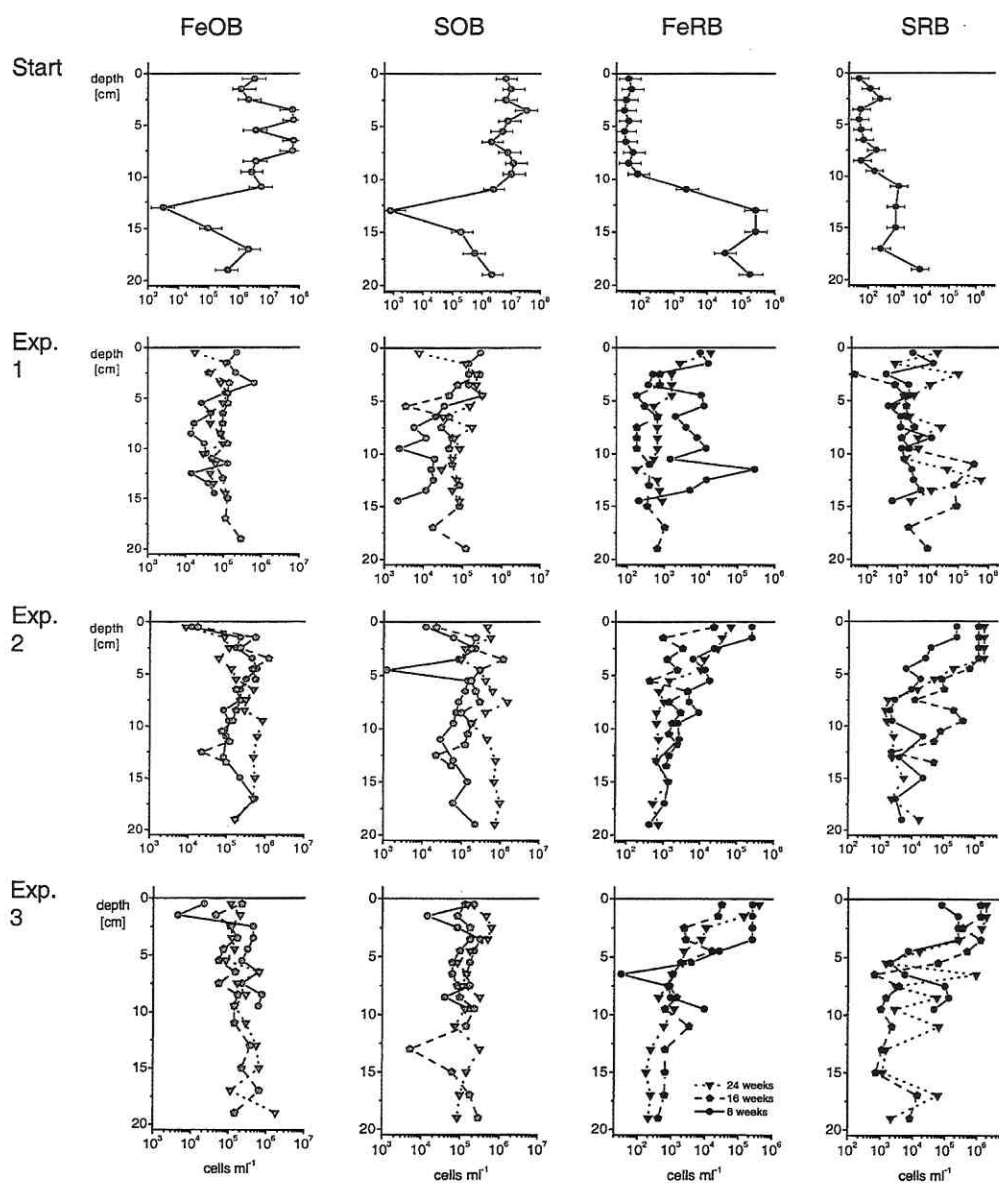


Fig. 6: Populations of culturable iron-oxidizing, sulfide-oxidizing, iron-reducing and sulfate-reducing bacteria. Error bars in start values show 95% confidence intervals. Since they were similar throughout, they were omitted in Experiment 1-3 for clarity. Note different scale for anaerobes.

However, after 8 weeks FeRB dominated over SRB in the upper 3 cm which was reversed after 16 weeks. After 24 weeks the SRB profile became irregular, and in addition to the surface maximum abundances $\geq 10^5 \text{ ml}^{-1}$ were found in several layers. Thus the treatment with algal material induced a succession of iron-reducing and sulfate-reducing populations which shifted more rapidly towards sulfate reducers in Exp. 2 with neutral overflowing water.

In Exp. 1, FeRB increased to 10^4 ml^{-1} after 8 weeks in most layers and a maximum at 11-12 cm was still present. Numbers then declined again to 10^2 - 10^3 ml^{-1} except in the upper cm. SRB also increased over the whole profile and became more abundant than FeRB after 16 weeks. At this time a maximum with $>10^4 \text{ cells ml}^{-1}$ was present in 10-16 cm depth. After 24 weeks the same was found at 11-14 cm although the profile was irregular with additional maxima in other layers.

Potential Fe(III) reduction rates

Initially, two Fe(III) reduction zones with high potential rates ($>10 \mu\text{mol g ww}^{-1} \text{ d}^{-1}$) were found (Langner et al., submitted). In the experiments, the time course of Fe(III) reduction was non-linear and differed substantially between cores. Therefore, no uniform time span to determine rates seemed suitable, and non-linear regression could not be performed with 3 time points. As a compromise, Fe(III) reduction rates were determined in 3 ways for each incubation: a total rate obtained as linear regression from all time points, an initial rate (0 +6/7 days, equal to that determined from the first core), and an end rate (6/7 + 13/14 days) (Fig. 7).

If the 3 rates are similar, Fe(III) reduction was uniform over time. Higher initial rates indicate that Fe(III) reduction declined or Fe(II) even decreased during the assay. Higher end rates are due to lag phases in the beginning of the incubation.

Exp. 2 and 3 show similarities as well as differences, with broadly distributed activity after 24 weeks being the most obvious difference to Exp. 1. Maximum activities were similar to starting conditions ($13\text{--}18\ \mu\text{mol g}^{-1}\text{d}^{-1}$). After 8 weeks, initial Fe(III) reduction rates were generally highest. Exp. 2 showed elevated activity near the surface and a distinct increase with depth below 10 cm. The latter was not observed in Exp. 3 since the core was only 10 cm long. After 16 weeks the rates of Exp. 2 were scattered and in many cases loss of Fe(II) occurred. Exp. 3 exhibited a pronounced maximum at the surface. Below this all rates were close to zero, indicating that no significant Fe(III) reduction occurred at any time of the assay. Rates obtained after 24 weeks differed widely but showed the same trends. Initial values were lowest, and end rates were mostly maximal, indicating that Fe(III) was most rapidly reduced after prolonged incubation.

In Exp. 2 most rates were positive and rather high, especially between 5 and 15 cm. Exp. 3 showed initial loss of Fe(II) followed by high reduction rates. Below the maximum at 2 cm rates slightly decreased with depth. In Exp. 1, after 8 weeks initial rates were also highest, followed by a loss of Fe(II). Only the top cm showed low but consistent activity. After 24 weeks rates were zero at the surface, consistently low around 5 cm and high near the bottom of the core (13–15 cm). Sterile controls also sometimes showed activity, but high standard deviations, so the true abiotic activity remains unclear (data not shown).

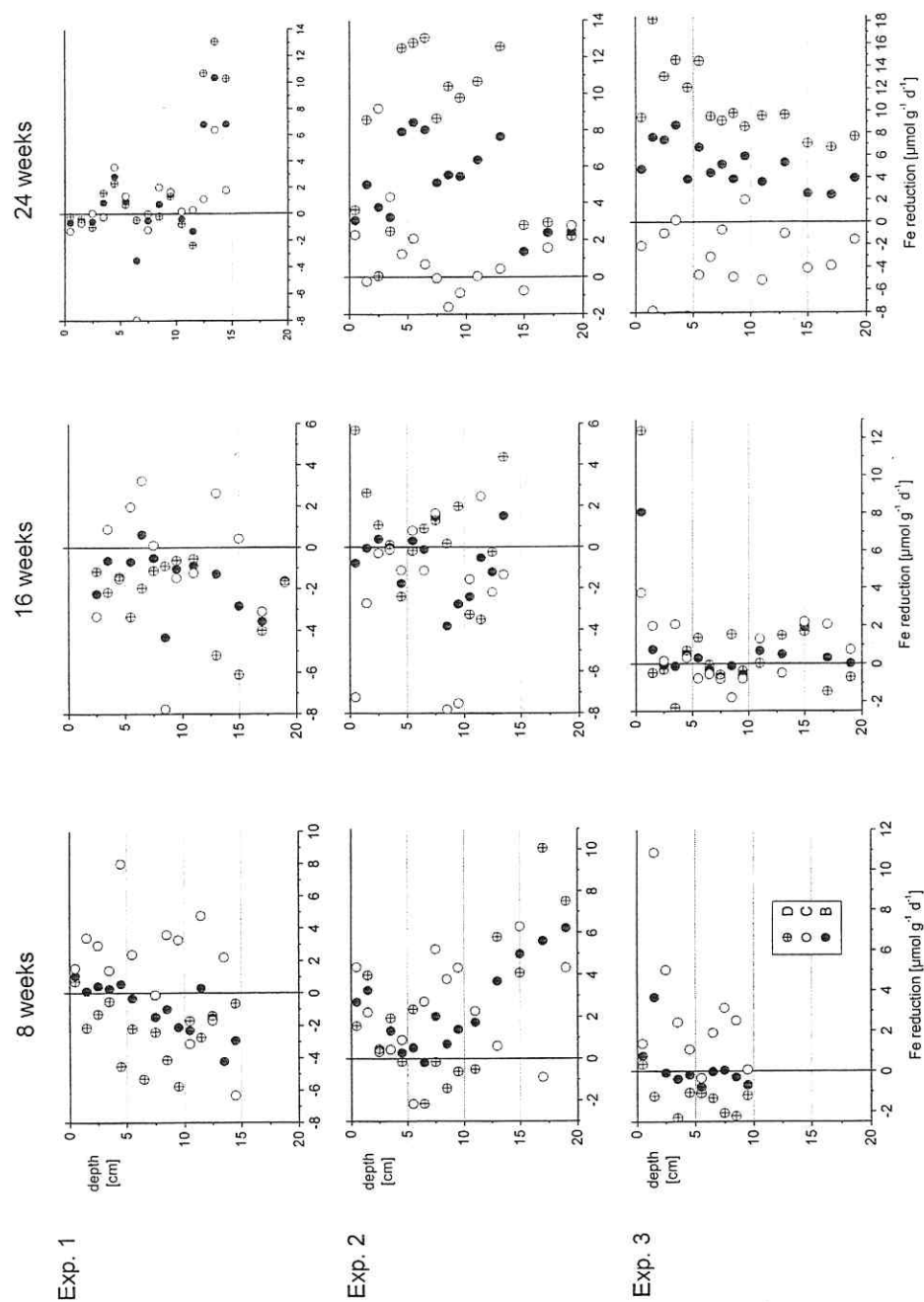


Fig. 7: Fe(III) reduction potential in the 3 experiments. Rates were calculated in 3 different ways: total rates from 3 time points (○, 6 and 13 days) (●), initial rates from the first 6 days (○) and end rates from 6 to 13 days (⊗).

Potential Fe(II) oxidation rates

Fe(II) oxidation was easily visible by the formation of brown precipitates, and often Fe(II) was almost depleted after 10-15 days of incubation. Initially Fe oxidation potential was between 14 and 23 mmol l⁻¹ g⁻¹ d⁻¹ with slightly higher values in the upper 5 cm. Some layers exhibited lag phases in oxidative activity, most obviously 2-3 and 10-12 cm. Fe(II) oxidation in poisoned controls was between 0 and 2.3 mmol l⁻¹ g⁻¹ d⁻¹ indicating that chemical oxidation accounted for max. 10% of the whole activity under these conditions.

During incubation the three treatments developed differently with respect to Fe(II) oxidation potential, especially in the upper 5 cm. In Exp. 2 and 3 activity below 10 cm was rather homogeneous and changed little with time whereas Exp. 1 developed irregular depth profiles. In Exp. 2 Fe(II) oxidation in the surface layer showed a pronounced lag phase, and maximum activities in this zone were only 23-45% of initial values (5-10 mmol l⁻¹ g⁻¹ d⁻¹). This corresponds to the minimum in FeOB abundance. However, in general Fe(II) oxidation and numbers of FeOB were not correlated. Poisoned controls oxidized 1.3-5.5 mmol l⁻¹ g⁻¹ d⁻¹. Exp. 3 where sediment was overflowed by acidic water also showed decreased Fe(II) oxidation at the sediment surface. This decline was less pronounced than in Exp. 2 (10-14 mmol l⁻¹ g⁻¹ d⁻¹ corresponding to 45-64% of initial activity). Again activity in poisoned controls was delayed and low (<1-6.6 mmol l⁻¹ g⁻¹ d⁻¹). Activity in deeper layers of Exp. 1 sometimes exceeded initial values. After 8 weeks a minimum was found at the surface which had disappeared after 24 weeks. Poisoned controls did not oxidize Fe(II) in the beginning of the assays, but after ca. 10 days incubation significant Fe(II) oxidation, sometimes as high as in live assays, was observed.

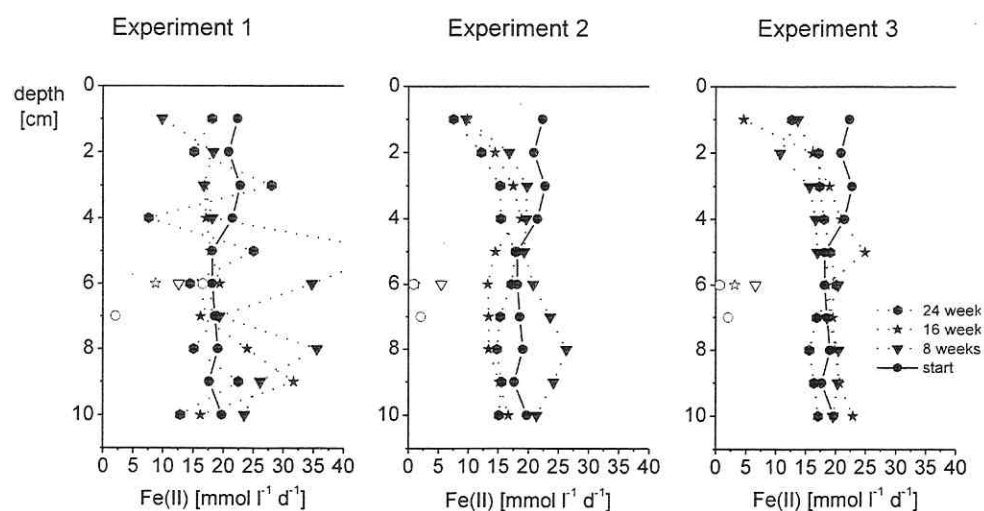


Fig. 8: Fe(II) oxidation potential in the upper 10 cm of the sediment cores. Open symbols represent sterile controls

DISCUSSION

The experiments showed that addition of easily degradable organic matter induced substantial biogeochemical changes in the sediments that could not be induced by overflow with neutral water alone (Exp. 1). It was evident from pH, E_H , reactive Fe profiles, reduced sulfur phases and microbiology that a reductive zone was established near the sediment surface, where alkalinity was generated by Fe(III) reduction and sulfate reduction.

Geochemical changes

The most significant geochemical changes in the sediments related to the addition of organic material and P are the accumulation of Fe(II) phases and sulfides near the sediment surface which were not observed in unamended cores. Similar findings were obtained by mesocosm studies for neutralization of acidic mining lakes (Frömmichen 2001, PhD thesis, Technical University of Dresden). Associated with mineralization of plankton biomass, Fe(III) reduction rates must have been high during the first 16 weeks of the experiments. High geochemically calculated rates of Fe(II) accumulation (at least $2.7 \mu\text{mol g-ww}^{-1}\text{d}^{-1}$) are in the same order of magnitude as Fe(III) reduction rates derived from porewater concentrations at the start of the experiments (Langner et al. submitted). However, the site of maximum Fe(III) reduction had obviously been shifted towards the sediment surface since more easily degradable organic matter was available there. A neutral pH value in the overflowing water had a beneficial effect on accumulation of Fe(II) phases. Compared with Exp. 3 (acid overflowing water) the Fe(II) maximum was located directly at the sediment surface whereas it was found at a depth of 1-2 cm after 8 weeks in Exp. 3. Studies by Langner and Friese (submitted) reveal that Fe(II) phosphate, vivianite, has formed due to P supplementation. Besides the appropriate geochemical milieu the presence of bonding partners is important for accumulation of Fe(II) phases. In untreated Lake Niemegk sediments high Fe(III) reduction rates did not result in significant Fe(II) enrichment although solubility conditions for vivianite were matched according to PHREEQC (Parkhurst 1995) calculations (Langner et al., submitted). Similar mining lake sediments in Lusatia also showed only weak Fe(II) accumulation as sulfides due to a lack of bonding partners (Peine et al. 2000). Sulfides that were detected in a later phase (8-24 weeks) of the experiments prove that sulfate reduction occurred and followed Fe(III) reduction in time which was more prominent in the earlier phase. Comparison of Fe(II)

accumulation with sulfide accumulation indicates that Fe(III) reduction was the dominant process and other Fe minerals than sulfides must have formed in substantial amounts. Laboratory experiments with pure Fe oxyhydroxides under neutral conditions showed additional Fe(II) carbonate formation (Schinzel et al. 1993). In a neutral mining lake also up to 10% siderite were formed (Langner et al. submitted).

Although the pH values increased in the reducing zones due to alkalinity generating processes, the observed dramatic changes in geochemical milieu and DOC porewater profiles over the whole depth of the sediment cores did not significantly correspond to the observed reducing zones or other geochemical processes. Especially in Exp. 1 and 2, DOC was not correlated to any geochemical parameter. Alternative explanations for the observed changes in pH might be the missing influence of acidic water from the underground as well as the somewhat variable composition of the starting material combined with mineral transformations of Fe hydroxides. Langner et al. (submitted) reported that pH profiles were (besides Fe(III) reduction) highly dependent on influences from the underground and on the transformation rate of schwertmannite to goethite. Geochemical modelling could partly explain the non-stationary situation of pH distribution by small manipulations of key parameters (Fe oxide transformation rate, pH of underground water, Fe(III) reduction rate; see Langner et al. submitted). Only in Exp. 3 the discussed turnover reactions during organic matter degradation are reflected in pH values and porewater DOC, Fe and SO_4^{2-} concentrations. Thus these parameters do not serve as clear indicators for microbial Fe(III) reduction and sulfate reduction in our experiments.

Microbial population changes

Phospholipid phosphate extractions revealed an increase in microbial biomass near the surface in supplemented cores and a second maximum at higher depth in all cores. Under our experimental conditions this can be most likely attributed to bacterial growth, although proliferation of fungi at the sediment surface can not be excluded. Contribution of plankton cells from the initial supplements is unlikely, since frozen and thawed material was used and sampling took place 8 weeks after supplementation. Phospholipid of dead cells undergoes substantial degradation within days in sediments both under aerobic and anaerobic conditions (White et al. 1979). The maxima which developed near the surface after addition of algal material are within the range reported for organically enriched sites (Dobbs and Findlay 1993) and which were also found in other acidic mining lake sediments when these were treated with organic materials for remediation purposes (Koschorreck et al., submitted). Conversion to cell numbers indicated that only a small fraction of total bacteria were cultured in our assays. This is partly due to the general limitations of selective cultivations. However, some groups that are likely to be important in this biogeochemical situation, like fermenters or aerobic acidophilic heterotrophs, were not considered in our study.

The correspondence of viable biomass with DOC values reflects degradation of POC and release of adsorbed organics. The fact that DOC was not quantitatively related to biomass or activity indicates that other processes than mineralisation have a strong influence on DOC profiles. Extremely high DOC values have also been found in other mining environments (Fortin and Beveridge 1997, Friese et al. 1998). Since natural DOC in mining lake sediment is mostly refractory humic-like material, a correspondence with POC degradation could also not be established (Blodau et al. 2000).

Although cultured bacterial populations have been reported to show poor correlation with in situ processes or measured activities (e.g. Gibson et al. 1987, Fortin et al. 2000), substantial correspondence between biogeochemical reactions and culturable populations of the respective bacteria has been observed in our study. The numbers of FeOB and SOB found in Lake Niemegek sediment are comparable to those from mine tailings (Fortin et al. 1995, Blowes et al. 1998) or bioleaching operations (Groudev and Groudeva 1993). Although some decline occurred in the beginning of the experiments, their abundance remained high despite anoxic conditions, elevated organic carbon concentrations and increasing pH values in the sediment. This can be due to the fact that some of them, like *Acidithiobacillus ferrooxidans* (formerly *Thiobacillus ferrooxidans*) are facultative anaerobes that are able to use Fe(III) as electron acceptor with S^0 as electron donor (Brock and Gustafson 1976). At least in later stages of the experiment, S^0 might have been present as a partially oxidized product of microbial sulfate reduction.

The marked decrease of FeOB near the surface in Exp. 2 must be attributed to the concomitant presence of organic matter and neutral overflowing water, since neutral water alone (Exp. 1) or organic matter combined with acidic pH (Exp. 3) had no significant effect. The decrease in FeOB numbers corresponds to the pronounced lag phases in the Fe oxidation assays, indicating that some proliferation is involved before maximum rates are reached.

In contrast to FeOB, SOB populations near the surface of Exp. 2 were lower only after 8 and 16 weeks, but increased after 24 weeks. A possible explanation is the regeneration of sulfides by microbial sulfate reduction which obviously occurred at that time. The fact that in situ pH at that time was markedly higher than that of the culture medium indicates a wide pH tolerance of the SOB.

The initially low numbers of FeRB are comparable or even lower to those reported from other acidic mine drainage environments under similar conditions (Friese et al. 1998). Unfortunately we did not count acidophilic Fe(III) reducers (Küsel et al. 1999, Bridge and Johnson 2000) that can be expected to make up a significant part of the population in such environments. Therefore we do not know if the population shifted from acidophilic towards more neutrophilic organisms during the 24 weeks of the experiments. The FeRB densities of in the active Fe(III) reducing zones are high even compared to other active Fe(III) reducing environments (Jones et al. 1983, Nielsen et al. 1997) suggesting optimal conditions for these organisms. The prolonged dominance of FeRB over SRB in Exp. 3 can be a consequence of the more acidic conditions in this experiment. Fe(III) reduction is energetically favoured over sulfate reduction under acidic conditions (Postma and Jakobsen 1996) which might have stimulated FeRB activity and proliferation. As a consequence, FeRB in general should be less sensitive to low pH than SRB. However, the contribution of truly acidophilic Fe reducers like *Acidiphilium* to culturable FeRB abundance in our assay must be of minor importance, since they normally do not grow at pH 6 and above.

In contrast to studies from oxic and acidic mine tailings where SRB populations were high despite no indices of sulfate reduction were detected (Fortin et al. 2000), numbers of SRB were initially low in Lake Niemegk sediment, which is possibly due to less bacteria input from the surrounding sandy soil. The increase in SRB populations together with the accumulation of reduced inorganic sulfides in Exp. 2 and 3 give clear evidence of microbial sulfate reduction although this was not directly measured with radiotracer ($^{35}\text{S SO}_4^{2-}$) assays.

Microbial activities

Potential Fe(II) oxidation was inhibited in the reducing zone, especially when the pH of the overflowing water was neutral. Since the assay itself was performed in a highly oxidic and acidic medium, this implies that microbial alkalinity generation can not be reverted easily by short-term oxygen contact or acidity input due to mixing events in a lake. Although potential Fe oxidation was very homogeneous and stable below 5 cm in all experiments, rapid reoxidation and re-acidification due to this biological potential is unlikely in such a sediment unless massive erosion of more than the upper 5 cm of the sediment will occur.

Fe(III) reduction rates in the experiments were high compared to similar Fe(III) reducing environments (Blodau et al. 1998). However, loss of Fe(II) during incubation was also often observed despite handling in oxygen-free atmosphere. A possible explanation would be the formation of solid Fe(II) phases at the inner surface of the glass vials which was probably not adequately sampled by stirring and shaking of the slurry. The maximum rates of Fe(III) reduction in Exp. 2 and 3 were not substantially higher than in deep layers of Exp. 1 after 24 weeks or before the experiment in May 1998 ($10\text{--}11\ \mu\text{mol g}^{-1}\text{ d}^{-1}$, Langner et al. submitted). Several factors may be responsible for this unexpected result: first, input of reactive Fe over time might have been similar in the lake due to extremely high sedimentation rates (Langner et al. submitted). Secondly, a depletion of bioavailable Fe occurred after 16 to 24 weeks (Figure 4), so that sulfate reduction became competitive. This fits well with the pattern of Fe(III) reduction activity in the assays after 24 weeks. Rates increasing with prolonged incubation show that a potential had been revitalized by Fe(III) addition that was not present initially. Thirdly, the high Fe(III) reduction rates measured in deeper sediment layers in May 1998 might have also been due to reactive organic carbon supply by a sedimented algal bloom and thus be the result of similar conditions in

the lake and experimental sediment. Woelfl et al. (2000) have reported the occurrence of short-term mass developments of phytoplankton in Lake Niemeck that might not be detected by monthly routine sampling of the water column. Generally our Fe(III) reduction potentials may overestimate real rates not only due to high Fe(III) addition or through physical disturbance of the sediment (Phelps et al. 1994), but also due to the presence of molecular hydrogen in the gas phase of the assays.

Stimulation of Fe(III) reduction by H_2 has been observed in incubations with mining lake sediment (Küsel et al. 2000). Some Fe(III) reduction via sulfide or reduced humic materials (Lovley et al. 1996, Nevin and Lovley 2000) could also have occurred, since sterile controls sometimes showed Fe(II) production, especially after 24 weeks. However, this is unlikely to play a major role in our assays, since the original sediment was diluted with a large volume of $Fe(OH)_3$ slurry. Moreover, the high concentrations of solid Fe(II) phases but low sulfide concentrations indicate that the net Fe(III) reduction over the whole experiment was substantially higher than sulfate reduction. This was also reported from other acid mine drainage environments (Peine et al. 2000). It also indicates that other Fe(II) minerals than sulfides must have formed in our case, predominantly vivianite (Langner and Friese, submitted). Fe(II) mineral formation is an important process in mining lake neutralization, since if reduced Fe diffuses out of the sediment it will be reoxidized in the water column, creating an acidic iron cycle (Peine et al. 2000).

CONCLUSIONS

Our results suggest that biogeochemical processes induced by sedimentation of reactive organic matter during flooding of a mine pit will play a crucial role in the desired neutralization. A productive river with high nutrient and plankton concentrations will therefore have a beneficial effect by establishing an active alkalinity-producing zone in the sediment of the lake that can serve as buffer against further input of acidity with the groundwater flow or short-term oxygenation of the sediment surface. This alkalinity-producing zone is equally well established when overflowing water is acidic, indicating minor importance of lake water pH, and proliferation of iron and sulfate reducing bacteria is involved in its formation. Both iron reduction and sulfate reduction contribute to alkalinity generation, with sulfate reduction following Fe(III) reduction in time and space. Reoxidation of Fe(II) is inhibited in this zone. Sufficient bonding partners for Fe(II), in our case unusually high P concentrations, are necessary to prevent diffusion of soluble Fe(II) to oxic zones and subsequent loss of alkalinity due to reoxidation. Despite the limitations of selective cultivation methods, geochemical processes and responsible culturable populations were clearly correlated. The carrying capacity of this biological buffer or the exact influence on the time scale of neutralization can not be inferred from our semi-batch experiments and deserves further investigation.

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3 Zusammenfassung der Ergebnisse

3.1 Zusammenfassung der Einzelarbeiten

Manuskript (1)

Im ersten Manuskript werden die geochemischen Ausgangssituationen von Sedimenten in zu flutenden Bergbaurestseen zusammengefaßt, was besonders die Erfassung der dominant wirkenden frühdiaagenetischen Prozesse beinhaltet. Die Ergebnisse der Untersuchungen zeigen, dass sich die Zusammensetzung der Seesedimente des neutralen und sauren Restsees sehr ähnelt. Sie bestehen zum überwiegenden Teil aus Eisenhydroxiden, die im oberen Bereich schlechter kristallisiert sind als in tieferen Sedimentschichten. In sauren Restseesedimenten konnten mineralogische und geochemische Hinweise auf die Existenz von Schwertmannit gefunden werden. Im Gegensatz zum sauren Restsee ist es in den neutralen Restseesedimenten zu einer Bildung der authigenen Minerale Siderit und Eisensulfid gekommen.

Während die geochemischen Verhältnisse in den neutralen Restseesedimenten im Untersuchungszeitraum von einem Jahr gleichbleibend sind, zeigen die Porenwasserprofile im sauren Restsee innerhalb kurzer Zeiträume zum Teil instationäre Zustände an, was sich besonders in den Milieuparametern über die Teufe widerspiegelt. Sowohl geochemisch als auch mikrobiologisch konnten ausgeprägte Zonen von Umsetzungsprozessen festgestellt werden, bei denen organische Substanz unter Fe(III)-Reduktion abgebaut wird. Die untere Zone zeigte einen deutlichen pH-Anstieg. Je nach Abbaurate wird durch die Reduktion eine unterschiedliche Menge an Alkalität produziert, die zu einer Instabilität des Minerals Schwertmannit führt. Geochemische und mineralogische Untersuchungen zeigten verbunden mit geochemischen Berechnungen durch PHREEQC, dass es in diesen Zonen zu einer Umwandlung von Schwertmannit hin zu dem

stabileren und besser kristallineren Goethit kommt. Dies erzeugt eine Pufferung der ansteigenden pH-Werte.

Geochemische Modellierungen mit CoTReM konnten die aufgezeigten Prozesse anhand der pH-Profile reproduzieren. Dabei standen besonders der Abbau der organischen Substanz mittels Fe(III)-Reduktion und die Transformation von Schwertmannit zu Goethit im Vordergrund. Zum einen konnten die prägnanten Prozesse allgemein durch die Modellierung verschiedener geochemischer Parameter dargestellt und auf zwei spezielle Untersuchungsbeispiele übertragen werden. Mit der Modellierung bestätigten sich die geochemisch berechneten Fe(III)-Reduktionsraten aus den Fe-Porenwasserprofilen, die als mikrobiologisch bestimmte potentielle Raten in der selben Größenordnung lagen. Ein wesentliches Ergebnis der Modellierung war das Aufzeigen der instationären Zustände der geochemischen Variablen. Während die Eisen- und Sulfatkonzentrationen in den Porenwässern mit fortlaufender Umsetzung stetig anstiegen, erreichten die pH-Verhältnisse zu einem Zeitpunkt (Okt. 1998) Gleichgewichtszustand. Weiterhin konnte festgestellt werden, dass die geochemischen Parameter durch zeitliche Variationen von Randbedingungen, wie die Höhe der Umsetzungsraten und Eintrag von Stoffen, sowohl aus tieferen Sedimentschichten als auch aus dem Bodenwasser, wesentlich beeinflusst werden.

Manuskript (2)

Dieses Manuskript basiert wesentlich auf Auswertungen von Laborexperimenten, die zur Erfassung der P-Mobilität in Sedimenten während und nach der Flutung eines Tagebaurestsees mit Flußwasser, durchgeführt wurden. Die Laborexperimente zeigen, dass innerhalb von 16 Wochen fast der gesamte an $\text{Fe}(\text{OH})_3$ adsorbierte Phosphor zu Vivianit umgesetzt worden ist, sofern gut abbaubarer organischer Kohlenstoff zur Verfügung steht. Dies beruht auf der

Eisenreduktion, die durch den Abbau von zugegebenem Algenmaterial initiiert worden ist und für diese Versuche von Wendt-Potthoff and Langner (Kap. 2.3) näher beschrieben werden konnte. Die Milieubedingungen im überstömenden Bodenwasser wie der pH-Wert und der Anteil an gelöstem Sauerstoff sind bei diesem Prozess von untergeordneter Bedeutung. Lediglich der Umsetzungsort hat sich unter sauren Verhältnissen anfänglich (nach 8 Wochen Inkubation) um einen Zentimeter ins Sediment hineinverschoben, während er bei neutralem Bodenwasser direkt an der Sedimentoberfläche liegt. Sowohl bei sauren als auch bei neutralen Bodenwasserverhältnissen wird ähnlich viel Eisen reduziert und damit Phosphor freigesetzt. Nur die Bildung von Eisenphosphat ist stark von den pH Bedingungen abhängig, was durch thermodynamische Gleichgewichtsberechnungen mit PHREEQC bestätigt werden konnte. Da der pH-Wert in den oberflächennahen Sedimentschichten bei gleicher Eisenreduktion besonders durch die molekulare Diffusion von H^+ beeinflusst wird (Langner et al. Kap. 2.1), wirkt sich das Bodenwasser bei sauren Verhältnissen hemmend auf die Ausfällung von Vivianit aus. PHREEQC-Berechnungen an Porenwasserdaten zeigen, dass sich bei pH=3 im Bodenwasser in der obersten Sedimentschicht ein thermodynamisches Gleichgewicht zu Vivianit eingestellt hat. Die gemessenen SRP-Konzentration im Porenwasser von 100 mmol/l sind wesentlich höher als bei neutralem Bodenwasser (19 mmol/l). Damit ergibt sich, dass der pH-Wert einen entscheidenden Einfluß auf den SRP-Flux vom Sediment ins Bodenwasser hat. Der anhand von Porenwassergradienten an der Sedimentoberfläche berechnete SRP-Flux erreicht nach 8 Wochen Inkubation Maximalwerte, die bei saurem überströmenden Wasser $0,2 \text{ mmol m}^{-2} \text{ d}^{-1}$ und bei neutralem Bodenwasser $0,02 \text{ mmol m}^{-2} \text{ d}^{-1}$ beträgt und sich im weiteren Verlauf der Experimente verringert.

Die Bindungsform von Phosphor hat sich während der Inkubation bei allen Experimentansätzen über die gesamte Sedimenttiefe verändert. Bei Startbedingungen waren bis zu 85 % Phosphor mit Bicarbonat-Dithionit löslich (P-Fraktionierung in Anlehnung an Psenner et al. 1984) feststellbar, der nach 24 Wochen fast vollständig in der NaOH-Fraktion nachgewiesen werden konnten. Dies kann ein Ergebnis des Umwandlungsprozesses von Schwertmannit zu Goethit sein. Die Ergebnisse von Langner et al. (Kap 2.1) an den selben Sedimenten stärken diese These. Dieser Umwandlungsprozess wurde von Bigham et al. (1990) unter Auflösung des Schwertmannits nachgewiesen. Der adsorbierte Phosphor kann dabei freigesetzt werden und neue Bindungen eingehen, die mit NaOH in Lösung gebracht werden können.

Die Bildung von Sulfiden hat sich innerhalb der Inkubation auch unter anoxischen Verhältnissen im überströmenden Wasser nicht erhöhend auf die P-Konzentrationen im Bodenwasser ausgewirkt, da Eisen in hohen Konzentrationen als Bindungspartner für P zur Verfügung steht. Allerdings können keine langfristigen Aussagen dazu getroffen werden.

Überträgt man die Ergebnisse der Experimente zu den Flutungsszenarien auf den entstehenden Bergbausee, so kann bei einem schnellen pH-Anstieg im Seewasser von wesentlich geringeren SRP-Flüssen aus dem Sediment ins Wasser ausgegangen werden als bei natürlichen eutrophen Seen mit saisonal aneren Verhältnissen im Hypolimnion. Die einmalige P-Zufuhr über das Flutungswasser führt zu sehr viel geringeren Phosphorgehalten im Sediment als die in den Versuchen simulierten. Außerdem ist das Angebot an Eisen in den Sedimenten ausreichend, um den freigesetzten Phosphor zu binden. Zum einen bieten die vorwiegend aus Eisenhydroxiden bestehenden Sedimente mögliche Adsorptionsplätze für Phosphor zum anderen sind die Fe-Porenwasserkonzentrationen so hoch, dass bei entsprechenden pH-Bedingungen Eisenphosphat ausgefällt werden kann und Phosphor dem internen Seekreislauf somit entzogen wird. Eine mit

dem SRP-Flux ins Freiwasser viel diskutierte Fe-Limitation liegt in diesem Sedimentsystem nicht vor. Die Neukristallisation der Eisenhydroxide in Goethit und die Fixierung von Phosphor an schwerer lösliche Verbindungen vermindert zusätzlich die Reaktivität von Phosphor und die damit im Zusammenhang stehende Freisetzung in die Wassersäule.

Manuskript (3)

Das dritte Manuskript untersucht das Zusammenwirken von geochemischen und mikrobiologischen Entwicklungen in Bergbaurestseesedimenten bei der Zugabe von organischen Kohlenstoff. An Hand der Ergebnisse aus den Inkubationsversuchen läßt sich übereinstimmend feststellen, dass die biogeochemischen Prozesse, die durch das angebotene Planktonmaterial initiiert werden, zu wesentlichen Veränderungen in den Sedimenten führen und einen entscheidenden Einfluß auf die Alkalitätsproduktion im Sediment haben.

Der dem Sediment zugegebene organische Kohlenstoff wird relativ unabhängig von den Milieubedingungen im Bodenwasser unter Reduktion von Fe(III) abgebaut und führt zur Lösung der Eisenhydroxide und zur Anhebung der pH-Werte. In den Experimenten mit zugegebenen Kohlenstoff konnte in einer ersten Periode (bis zu 16 Wochen) die Ausbildung von Fe(III)Reduktionszonen in oberflächennahen Schichten festgestellt werden, die von einer hohen Anzahl an eisenreduzierenden Bakterien und hohen potentiellen Fe(III)-Reduktionsraten begleitet waren. Außerdem konnte die Anreicherung von Fe(II)-Verbindungen nachgewiesen werden, die maximalen Raten von $2,7 \text{ mmol Fe(II) g}^{-1}\text{ww d}^{-1}$ entsprechen. Diese sind mit den berechneten Fe(III)-Reduktionsraten zu Startbeginn der Experimente vergleichbar. In einer zweiten Periode spielte die Sulfatreduktion eine zunehmende Rolle und ersetzte die Fe(III)Reduktion zum Ende der Experimente. Sulfidanreicherungen mit bis zu $12 \text{ mg S g}^{-1}\text{dw}$ und

die höchste Anzahl an sulfatreduzierenden Bakterien konnte in den Reduktionszonen nachgewiesen werden. Die Reoxidation von Fe(II) wurde in diesen Zonen durch eine "Leckphase" gehemmt. In den Reduktionszonen steigen die pH-Werte an, die jedoch nur effizient sind, sofern Bindungspartner wie zum Beispiel der mit in Lösung gegangener Phosphor oder reduzierter S zur Verfügung steht. Durch die Festlegung kann das gelöste Fe(II) nicht mehr in oxische Zonen diffundieren und durch Reoxidation zur Bildung von neuer Acidität führen. Die geochemischen Parameter des Porenwassers pH, Eh, DOC, Fe und Sulfat zeigen im Gegensatz zu den Parametern in der Festphase keine signifikanten Korrelationen sowohl zu den mikrobiologischen Parametern als auch zu den aufgezeigten Prozessen. Sie sind damit von untergeordneter Bedeutung bei der Auswertung der Ergebnisse zur P-Mobilität.

3.2 Zusammenfassung der Ergebnisse in Hinblick auf das Gesamtthema

Alle drei Manuskripte befassen sich mit Untersuchungen zu frühdia genetischen Prozessen in jungen Bergbaurestseesedimenten bei der Flutung eines Tagebaus in Mitteldeutschland mit nährstoffreichem Flußwasser und deren Wirkungen auf die Wasserqualität der entstandenen Seen. Hierzu zählen besonders die Prozesse der Eisenumsetzungen, die wesentlich den pH-Wert in den Sedimenten und die Mobilität von Phosphor steuern.

Durch das zugeführte Flußwasser wird das bereits vorhandene saure Restseewasser neutralisiert und die anfänglich hohen Konzentrationen an Fe werden durch die Ausfällung von Eisenhydroxiden extrem verringert. Während dieses Prozesses wird ein großer Teil an mitgeführtem Phosphor adsorbiert und gelangt durch Absinken der Eisenflocken in das

Seesediment. Das mit dem Flußwasser eingetragene gut verfügbare organische Material wird von eisenreduzierenden Bakterien als Energiequelle genutzt und unter Fe(III)Reduktion abgebaut. Der adsorbierte Phosphor und der aus der organischen Substanz stammende Phosphor wird freigesetzt und kann bei entsprechenden geochemischen Milieubedingungen als Fe(II)-Phosphat festgelegt werden.

Der pH-Wert im Porenwasser wird wesentlich durch die Intensität der Prozesse der Eisenreduktion, durch die Umbildung von Schwertmannit zu Goethit und durch den Einfluß von saurem Wasser aus dem Untergrund und/oder von sauren Bodenwasser bestimmt. Wird davon ausgegangen, dass das Seewasser schnell neutralisiert wird und der Einfluß der sauren Verhältnisse im Untergrund durch einen dem See entgegengesetzten Wasserstromgradienten nahezu ausgeschlossen wird, wirken sich die beiden Eisenumsetzungen dominant auf die pH-Entwicklung aus.

Während die Intensität der Eisenreduktion durch die Abbauprozesse mehr saisonal bedingt ist, wird die Intensität der Umsetzung von Schwertmannit zu Goethit neben der produzierten Alkalität besonders von der Menge des vorhandenen Schwertmannit bestimmt. Der unter sauren Verhältnissen gebildete Anteil an Schwertmannit nimmt mit der Zeit ab, so wie es in tieferen Sedimentschichten aufgezeigt werden konnte, und führt zu einem schnelleren Anstieg der pH-Werte. Dieser reguliert wiederum die SRP-Konzentrationen im Porenwasser, da diese im thermodynamischen Gleichgewicht zu Vivianit stehen. Eine Limitation von Fe durch die Bindung von neu gebildetem Sulfid ist aufgrund der hohen Fe-Konzentrationen im Porenwasser und in der Festphase nicht zu erwarten, da auch die hohen Sulfidbildungsraten erst im Anschluß an die Fe(III)Reduktion festgestellt werden konnten. Unter pH Verhältnissen von 6-7 im Sediment ist der aus dem Porenwassergradienten bestimmte SRP-Flux ins Bodenwasser auch unter aneroben

Bedingungen sehr gering und die mögliche Bindungskapazität für Phosphor besonders groß, so dass die Sedimente eher als Senke für eingetragene P-Verbindungen wirken.

Zusammenfassend konnte durch die Ergebnisse erstmalig gezeigt werden, dass in jungen Sedimenten saurer Bergbaurestseen eines ehemaligen Braunkohletagebaus sehr instationäre geochemische Zustände herrschen können.

Die Untersuchungen wurden an 6 bis 8 Jahre jungen Bergbaurestseesedimenten durchgeführt. Bisher sind nur Ergebnisse vergleichbarer Untersuchungen an wesentlich älteren Restseesedimenten bekannt (Frömmichen 2001, Peine et al. 2000, Blodau et al. 1998, Peine 1998, Friese et al. 1998). Die zeitliche Variabilität der verschiedenen geochemischen Zustände in den jungen Sedimenten wird besonders durch die Änderung der Parameter des Angebots an mikrobiell verfügbarer organischer Substanz und des Eintrags von H^+ aus dem Untergrund initiiert, die auf die Dynamik der Prozesse einen großen Einfluß haben. Im Gegensatz zu älteren sauren Restseen können die Fe-Umsetzungsprozesse, die von ihrer Art vergleichbar nachgewiesen werden konnten (Frömmichen 2001, Meier et al. 2001, Peine et al. 2000, Blodau et al. 1998, Friese et al. 1998, Peine 1998), in den Sedimenten extremen Intensitätsschwankungen unterliegen. Die Umsetzungsprozesse in den sauren restseesedimenten und die geochemisch instationären Zuständen konnten erstmalig durch eine geochemische Modellierung mit CoTReM nachvollzogen werden.

Junge Sedimente des neutralen Restsees desselben Tagebauggebietes, bei den von ähnlichen Randbedingungen ausgegangen werden kann, weisen im Gegensatz dazu stationäre geochemische Zustände auf und sind in ihrer Diagenese weiter entwickelt als die von jungen sauren Restseen.

Mit den erbrachten Ergebnisse kann somit auch ein Beitrag hinsichtlich der Aufklärung zur geochemischen Entwicklung in Sedimenten der Restseen geleistet werden.

Weiterhin wurde innerhalb dieser Arbeit der Einfluß der Seesedimente auf die Trophieentwicklung in Flutungsseen anhand der P-Verfügbarkeit wissenschaftlich prognostiziert. Bisher beruhten diesbezügliche Prognosen der mit Flußwasser gefluteten Seen im Stadium vor der Flutung eher auf Berechnungen und Analogieschlüsse, die sich auf wissenschaftliche Untersuchungen einzelner Thematiken bezogen. Auch wurden hinsichtlich Aussagen zur Trophieentwicklung von Seen Sedimente bereits gefluteter Seen ehemaliger Braunkohletagebaue untersucht, die jedoch das Stadium vom Bergbaurestsee zum Flutungssee unberücksichtigt lassen und damit die Qualität des Flußwassers für die Flutung nicht in Frage stellen (Hupfer et al., 1998). Somit kann eine Regulation der Seewasserqualität erst durch spätere Sanierungsmaßnahmen erfolgen. Die Ergebnisse dieser Arbeit beruhen auf einer kombinierten Methodik mikrobieller und geochemischer Untersuchungen, die sich aus biogeochemischen Zustandsuntersuchungen und Inkubationsversuchen an ungestörten Sedimentkernen der zu flutenden Bergbauseen zusammensetzt. Diese Ergebnisse lassen den Schluß zu, dass die einmalige Flutung der untersuchten Bergbaurestseen mit P-reichem Flußwasser nicht dazu führt, dass die Sedimente ein Potential für die Eutrophierung der Flutungsseen hinsichtlich der P-Verfügbarkeit bilden sondern eine Kapazität für den See darstellen, um P dem seeinternen Kreislauf zu entziehen und damit einer Eutrophierung des Sees entgegenwirken.

Im Gesamten leistet diese Arbeit einen wichtigen Beitrag zur Aufklärung der Sedimentdiagenese und damit auch zur Entwicklung der Wasserqualität entstehender Flutungsseen aus dem ehemaligen Braunkohletagebau.

4 Ausblick

Die Ergebnisse der Untersuchungen haben gezeigt, dass die Fe-Diagenese, die pH-Wertentwicklung in den Sedimenten wesentlich steuert, der einen entscheidenden Einfluß auf die Festlegung von P-Verbindungen hat. Für eine Verbesserung der Prognose sollte ein besonderer Wert auf die Bereitstellung einer umfassenden Datengrundlage für Modellrechnungen (z. B. mit CoTReM) gelegt werden, um die Möglichkeiten der vorhandenen Modelle voll auszuschöpfen.

Für die pH-Wertentwicklung ist die Erfassung der tatsächlichen Eisenreduktionsraten an Restseesedimenten notwendig. Ebenfalls sollten dafür die Sulfatreduktion und der Oxidation von gebildetem S^{2-} durch Fe(III) quantifiziert werden. Durch die Bestimmung der Schwertmannitanteile in den einzelnen Sedimentschichten können die Umsetzungsraten zu Goethit erfaßt werden. Diese Daten dienen der genaueren Berechnung für die pH-Wertentwicklung in den Sedimenten, die dann mit den bereits gewonnenen Ergebnissen eine quantitative Einschätzung zur P-Festlegung und -Freisetzung in den zu flutenden Restseen zulassen.

Um detailliertere Aussagen zur P-Mobilität gebundener P-Anteile der NaOH-löslichen Fraktionen treffen zu können, ist es notwendig die Bindungsformen dieser Fraktionen in den Sedimenten zu bestimmen. Dafür sollte auch das Bindungsvermögen des organischen Materials und von vorhanden Aluminiumoxiden untersucht werden. Eine qualitative Bestimmung der organischen Substanz ist darin eingeschlossen. Auch für die Erfassung der Gesamtabbauraten ist es wichtig den Anteil an mikrobiell gut verfügbarer Substanz zu bestimmen.

Um eine Übertragbarkeit der gewonnen Ergebnisse zur P-Mobilität in Bergbaurestseesedimenten auf andere Tagebaue und Flutungsszenarien zu ermöglichen, sind in einem ersten Schritt die

Ergebnisse der Laborexperimente auf Sedimente des bereits in Flutung befindlichen Tagebaus Goitsche zu verifizieren. Die Wirkung der wichtigsten Steuerfaktoren auf die P-Mobilität sollten anhand gezielter Modellstudien beschrieben werden. Diese bilden eine grundlegende Voraussetzung für die Übertragung der Erkenntnisse auf andere Systemzustände.

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6 Datenanhang

Sauerstoffgehalte

Teufe	Niemegk		Doebern	
	Apr 97	Okt 97	Apr 97	Okt 97
	O_2 mg l ⁻¹	O_2 mg l ⁻¹	O_2 mg l ⁻¹	O_2 mg l ⁻¹
mm				
-8	n.b.	n.b.	n.b.	8,40
-7	n.b.	n.b.	n.b.	8,40
-6	n.b.	n.b.	n.b.	8,40
-5	8,37	n.b.	n.b.	8,40
-4	8,16	9,23	9,61	8,30
-3	8,27	9,28	9,61	8,30
-2	8,48	9,36	9,47	8,30
-1	8,69	9,36	9,47	8,30
0	8,48	9,36	9,33	7,89
1	6,59	8,43	8,78	6,62
2	5,55	7,67	8,64	5,45
3	4,92	6,27	8,50	4,63
4	3,98	4,57	8,36	3,82
5	2,93	3,13	5,99	2,19
6	2,72	1,99	3,48	0,97
7	3,35	1,31	1,81	0,15
8	3,35	0,85	1,25	0,10
9	3,35	0,47	0,84	0,05
10	3,14	0,17	0,14	0,05
11	3,04	0,13	0	0,05
12	2,83	0,04	0	0
13	2,72	0,04	0	0
14	2,20	0,04	n.b.	0
15	2,51	0	n.b.	n.b.
16	2,41	0	n.b.	n.b.
17	2,41	0	n.b.	n.b.
18	2,20	0	n.b.	n.b.
19	2,09	0	n.b.	n.b.
20	1,88	0	n.b.	n.b.
21	1,67	n.b.	n.b.	n.b.
22	1,47	n.b.	n.b.	n.b.
23	1,15	n.b.	n.b.	n.b.
24	0,84	n.b.	n.b.	n.b.
25	0,63	n.b.	n.b.	n.b.
26	0,42	n.b.	n.b.	n.b.
27	0,21	n.b.	n.b.	n.b.
28	0	n.b.	n.b.	n.b.
29	0	n.b.	n.b.	n.b.
30	0	n.b.	n.b.	n.b.

n.b. - nicht bestimmt

Porenwasser

Niemeck, April 1997

Tiefe cm	pH	Eh mV	SRP $\mu\text{mol l}^{-1}$	NH_4^+ mmol l^{-1}	NO_3^- $\mu\text{mol l}^{-1}$	SQ^{2-} mmol l^{-1}	DOC mmol l^{-1}	Fe(II) mmol l^{-1}	Fe _{gas} mmol l^{-1}	Mn mmol l^{-1}	Ni $\mu\text{mol l}^{-1}$	As $\mu\text{mol l}^{-1}$	Zn $\mu\text{mol l}^{-1}$
-5			1,68	0,17	3069,00	25,53	2,05	n.b.	9,73	0,109	1,33	0,031	6,27
0	2,7	831	1,71	0,25	3,57	23,38	1,76	n.b.	13,32	0,100	1,81	0,039	12,24
1	2,7	825	1,61	0,27	3,85	32,81	1,53	n.b.	13,30	0,095	1,87	0,035	9,48
2	2,7	619	1,65	0,31	3,14	34,58	1,42	n.b.	17,65	0,111	2,04	0,032	8,11
3	2,8	599	1,74	0,31	2,57	34,90	2,14	n.b.	19,90	0,105	2,03	0,028	6,73
4	2,8	587	1,94	0,32	2,36	41,77	1,66	n.b.	22,28	0,116	2,10	0,028	7,65
5	2,9	573	1,81	0,35	1,57	40,63	2,16	n.b.	24,68	0,115	2,21	0,029	6,88
6	3,0	556	2,00	0,39	1,43	35,52	1,82	n.b.	28,82	0,123	2,32	0,025	7,34
7	3,0	542	2,03	0,40	1,28	42,81	1,95	n.b.	28,78	0,116	2,30	0,023	7,19
8	3,1	522	2,13	0,42	1,28	47,60	1,64	n.b.	30,03	0,128	2,32	0,021	9,18
9	3,2	516	2,29	0,42	1,50	46,88	1,57	n.b.	28,15	0,107	2,18	0,020	6,88
10	3,2	508	2,38	0,41	1,43	46,67	1,86	n.b.	36,05	0,133	2,42	0,020	8,72
11	3,2	513	2,45	0,40	1,50	45,10	2,05	n.b.	30,95	0,116	2,25	0,019	7,50
13	3,2	529	2,26	0,41	1,64	43,23	2,24	n.b.	30,75	0,114	2,25	0,019	8,87
15	3,2	519	2,32	0,41	1,71	47,19	1,81	n.b.	33,20	0,111	2,35	0,023	7,50
17	3,3	499	2,49	0,46	1,84	112,81	1,63	n.b.	34,44	0,088	2,52	0,023	7,34
19	3,3	491	3,52	0,45	1,57	52,92	1,71	n.b.	39,25	0,102	2,40	0,023	7,65
21	3,3	490	2,55	0,43	1,78	52,92	2,58	n.b.	37,91	0,094	2,33	0,021	7,34
23	3,4	471	2,65	0,44	2,21	53,65	n.b.	n.b.	34,06	0,076	2,16	0,020	6,27
25	3,5	432	2,71	0,46	1,50	n.b.	n.b.	n.b.	47,16	0,094	2,21	0,019	8,41
26	3,6	421	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	37,34	0,078	2,08	0,021	6,58

Niemeck, Juli 1997

Tiefe cm	pH	Eh mV	SRP $\mu\text{mol l}^{-1}$	NH_4^+ mmol l^{-1}	NO_3^- $\mu\text{mol l}^{-1}$	SQ^{2-} mmol l^{-1}	DOC mmol l^{-1}	Fe(II) mmol l^{-1}	Fe _{gas} mmol l^{-1}	Mn mmol l^{-1}
-5			1,13	0,24	n.b.	50,94	1,82	n.b.	8,34	0,090
1	2,9	467	1,71	0,59	n.b.	80,10	4,74	n.b.	29,21	0,106
2	3,3	421	2,16	0,66	n.b.	92,60	3,85	n.b.	32,95	0,105
3	3,2	422	2,20	0,59	n.b.	96,31	5,00	n.b.	1,62	0,112
4	3,3	436	2,68	0,58	n.b.	10,42	3,58	n.b.	40,26	0,113
5	2,9	454	2,91	0,58	n.b.	128,13	4,05	n.b.	48,45	0,120
6	2,9	454	2,97	0,62	n.b.	119,79	3,77	n.b.	53,66	0,119
7	2,9	445	3,45	0,64	n.b.	143,75	4,17	n.b.	57,85	0,128
8	3,0	435	3,55	0,56	n.b.	135,42	4,25	n.b.	58,13	0,116
9	3,1	426	3,71	0,54	n.b.	148,88	4,78	n.b.	61,25	0,119
10	3,3	402	3,81	0,59	n.b.	144,79	4,95	n.b.	61,55	0,116
11	3,4	383	3,62	0,56	n.b.	138,54	5,68	n.b.	63,79	0,110
13	3,1	406	4,23	0,61	n.b.	160,42	4,61	n.b.	69,05	0,110
15	3,0	427	4,39	0,59	n.b.	160,42	4,61	n.b.	73,57	0,108
17	3,0	407	4,75	0,84	n.b.	178,04	4,82	n.b.	74,96	0,101
19	3,0	427	4,75	1,09	n.b.	146,88	6,10	n.b.	78,82	0,095
23	3,0	412	4,71	1,15	n.b.	171,88	7,25	n.b.	77,45	0,088
26	3,1	379	4,68	1,10	n.b.	166,67	11,11	n.b.	78,63	0,082
29	3,2	352	4,88	1,18	n.b.	180,21	11,83	n.b.	83,68	0,094
32	4,0	325	5,59	1,28	n.b.	190,63	13,51	n.b.	80,78	0,074
37	4,5	299	5,00	1,26	n.b.	175,00	12,77	n.b.	85,66	0,073

Niemeck, Oktober 1997

Tiefe cm	pH	Eh mV	SRP $\mu\text{mol l}^{-1}$	NH_4^+ mmol l^{-1}	NO_3^- $\mu\text{mol l}^{-1}$	SQ^{2-} mmol l^{-1}	DOC mmol l^{-1}	Fe(II) mmol l^{-1}	Fe _{gas} mmol l^{-1}	Mn mmol l^{-1}
-5			1,36	0,11	n.b.	20,21	0,45	n.b.	4,12	0,082
1	3,3	500	1,23	0,49	n.b.	39,69	3,21	n.b.	27,40	0,108
2	4,1	388	1,97	0,74	n.b.	53,85	4,03	n.b.	42,65	0,110
3	3,3	336	2,23	0,84	n.b.	29,38	5,03	n.b.	50,58	0,113
4	5,1	253	2,68	0,91	n.b.	81,87	7,04	n.b.	56,83	0,114
5	5,4	189	3,23	0,99	n.b.	68,54	8,58	n.b.	65,58	0,120
6	5,5	175	3,16	1,00	n.b.	68,96	8,01	n.b.	64,61	0,117
7	5,4	195	3,10	0,96	n.b.	67,60	7,31	n.b.	61,12	0,112
8	4,8	274	3,55	1,11	n.b.	62,40	4,04	n.b.	74,15	0,137
9	4,0	343	2,91	1,12	n.b.	81,98	2,39	n.b.	73,10	0,146
10	4,1	350	3,20	1,03	n.b.	78,02	2,15	n.b.	69,66	0,142
11	4,4	332	2,81	0,86	n.b.	66,88	5,05	n.b.	60,87	0,127
13	3,9	364	3,07	0,88	n.b.	71,67	3,09	n.b.	66,94	0,144
15	3,9	412	3,16	0,81	n.b.	78,44	1,87	n.b.	70,52	0,155
17	3,6	423	2,97	0,80	n.b.	75,10	1,97	n.b.	67,08	0,145
19	3,5	422	2,71	0,69	n.b.	68,85	2,54	n.b.	62,29	0,132
23	3,4	440	3,04	0,71	n.b.	75,83	2,41	n.b.	68,18	0,139
26	3,4	429	3,00	0,69	n.b.	74,17	2,98	n.b.	64,99	0,129
29	3,6	412	3,10	0,66	n.b.	76,04	3,13	n.b.	67,85	0,129
32	4,1	354	n.b.	n.b.	n.b.	66,35	6,13	n.b.	59,03	n.b.

Niemeck, Mai 1998

Tiefe cm	pH	Eh mV	SRP $\mu\text{mol l}^{-1}$	NH_4^+ mmol l^{-1}	NO_3^- $\mu\text{mol l}^{-1}$	SQ^{2-} mmol l^{-1}	DOC mmol l^{-1}	Fe(II) mmol l^{-1}	Fe _{gas} mmol l^{-1}	Mn mmol l^{-1}
-5			0,97	0,19	2141	7,12	0,79			
1	2,7	578	1,23	0,31	9,28	34,48	4,55	14,29	16,16	0,148
2	2,8	574	1,29	0,31	7,85	32,29	3,98	14,82	15,84	0,149
3	2,8	561	1,36	0,40	4,21	36,77	2,97	17,55	18,63	0,164
4	2,9	538	1,42	0,46	8,21	40,83	3,96	22,63	23,81	0,163
5	2,9	536	1,68	0,46	4,85	41,46	n.b.	22,32	23,48	0,163
6	2,9	538	1,36	0,48	4,14	41,77	3,36	23,60	24,07	0,161
7	2,9	532	1,42	0,49	5,14	42,92	2,96	23,68	24,85	0,167
8	3,0	529	1,49	0,49	3,71	42,92	2,65	24,72	26,04	0,167
9	3,0	520	1,49	0,53	5,42	43,13	2,62	25,58	26,35	0,159
10	3,5	508	1,52	0,56	3,50	45,31	2,46	28,17	28,30	0,159
11	4,3	446	1,91	0,64	5,92	51,04	3,89	34,21	35,30	0,153
13	4,8	352	2,07	0,71	5,57	50,73	4,36	34,87	36,54	0,145
15	4,6	284	2,29	0,71	4,85	53,23	3,86	37,08	38,58	0,141
17	3,8	301	2,26	0,74	4,14	52,81	3,16	40,27	40,97	0,141
19	3,7	387	2,03	0,70	4,71	56,77	3,26	41,61	43,81	0,138
21	3,5	401	2,32	0,71	4,71	57,60	3,28	43,72	44,30	0,136
23	3,4	420	2,36	0,69	4,84	58,38	2,83	42,42	45,14	0,133
25	3,2	437	2,39	0,68	4,71	58,13	3,08	41,74	41,65	0,119
27	3,2	456	2,36	0,71	3,57	60,31	2,45	44,39	45,19	0,124
29	3,2	458	2,39	0,71	4,00	59,90	2,51	46,25	44,35	0,121
31	3,2	456	2,28	0,67	3,85	56,25	3,47	45,03	43,94	0,117
33	3,2	461	2,28	0,71	5,78	56,15	3,38	44,28	43,21	0,114
35	3,2	456	2,23	0,67	5,42	55,73	3,36	41,50	41,74	0,111
37	3,3	451	2,20	0,69	10,71	55,31	3,41	40,30	40,72	0,106
39	3,3	406	2,29	0,72	4,50	55,63	4,89	40,95	41,70	0,104

Porenwasser

Doebern, April 1997

Teufe cm	pH	Eh mV	SRP $\mu\text{mol l}^{-1}$	NH_4^+ mmol l^{-1}	NO_3^- $\mu\text{mol l}^{-1}$	SO_4^{2-} mmol l^{-1}	DOC mmol l^{-1}	Fe mmol l^{-1}	Mn mmol l^{-1}	Ni $\mu\text{mol l}^{-1}$	As $\mu\text{mol l}^{-1}$	Zn $\mu\text{mol l}^{-1}$
-5	n.b.	n.b.	n.b.	n.b.	n.b.	8,77	n.b.	0,03	0,031	n.b.	0,221	<0,03
1	6,3	276	0,71	0,15	0,71	11,29	1,30	0,87	0,046	0,221	<0,13	0,29
2	6,2	276	0,71	0,14	0,71	11,98	1,27	0,33	0,066	0,307	<0,13	0,66
3	6,2	246	0,71	0,19	0,86	12,60	1,47	1,73	0,038	0,273	<0,13	0,40
4	6,6	176	0,97	0,33	1,93	15,63	2,60	5,42	0,040	0,145	<0,13	<0,15
5	6,7	145	1,13	0,42	1,07	16,56	3,78	6,60	0,036	0,131	<0,13	<0,15
6	6,8	119	1,26	0,39	1,07	17,60	6,90	9,25	0,036	0,119	<0,13	<0,15
7	6,9	88	1,13	0,44	1,28	18,13	6,50	10,36	0,033	0,104	<0,13	<0,15
8	7,0	73	1,23	0,46	0,86	19,27	5,92	11,94	0,034	0,101	<0,13	<0,15
9	7,0	55	1,29	0,49	1,00	19,90	6,31	11,49	0,024	0,094	<0,13	<0,15
10	7,1	42	1,19	0,51	2,21	20,21	6,32	13,16	0,031	0,083	<0,13	<0,15
11	7,1	36	1,03	0,54	1,21	20,73	6,80	12,24	0,027	0,072	<0,13	<0,15
13	7,0	42	0,97	0,57	1,00	20,94	6,35	12,33	0,024	0,097	<0,13	<0,15
14	7,0	43	1,00	0,55	1,21	21,88	6,02	12,94	0,024	0,124	<0,13	<0,15
15	6,7	47	0,51	0,19	1,21	21,51	7,23	15,70	0,027	0,114	<0,13	<0,15
16	7,0	48	0,94	0,49	1,64	21,25	2,87	13,66	0,023	0,145	<0,13	<0,15
18	6,9	63	1,29	0,54	1,43	22,92	5,06	15,14	0,027	0,204	<0,13	<0,15
20	6,8	77	1,36	0,46	1,36	n.b.	5,50	15,00	0,029	0,204	<0,13	<0,15
22	6,7	84	1,49	0,45	2,14	21,77	5,16	13,78	0,031	0,256	<0,13	<0,15
24	6,7	103	1,23	0,41	2,43	23,85	3,10	12,53	0,034	0,221	<0,13	<0,15
25			1,19	0,43	2,14	23,75	0,00	13,51	0,035	0,221	<0,13	<0,15

Doebern, Juli 1997

Teufe cm	pH	Eh mV	SRP $\mu\text{mol l}^{-1}$	NH_4^+ mmol l^{-1}	NO_3^- $\mu\text{mol l}^{-1}$	SO_4^{2-} mmol l^{-1}	DOC mmol l^{-1}	Fe mmol l^{-1}	Mn mmol l^{-1}
-5	n.b.	n.b.	0,13	0,08	0,08	18,44	0,65	0,40	0,028
0	6,3	103	0,16	0,20	0,20	18,65	2,39	1,30	0,029
1	6,3	94	0,39	0,28	0,28	17,50	4,83	2,08	0,031
2	6,3	83	0,29	0,30	0,30	17,60	5,41	2,39	0,027
3	6,5	66	0,19	0,34	0,34	16,46	8,81	2,73	0,019
4	6,6	33	0,19	0,40	0,40	14,79	10,91	3,13	0,017
5	6,7	14	0,19	0,44	0,44	13,85	11,24	3,54	0,013
6	6,8	-50	0,29	0,46	0,46	12,92	10,57	3,37	0,011
7	6,8	26	0,23	0,46	0,46	12,92	8,49	3,34	0,010
8	6,9	-4	0,26	0,45	0,45	12,40	7,39	3,23	0,009
9	6,9	-6	0,26	0,50	0,50	11,46	6,13	3,04	0,007
10	6,9	-36	0,29	0,51	0,51	11,04	5,18	3,17	0,000
12	6,9	-25	0,29	0,50	0,50	10,94	4,57	2,91	0,006
14	7,0	-26	0,29	0,46	0,46	9,79	2,56	2,04	0,004
16	7,0	-20	0,36	0,42	0,42	9,65	3,01	2,33	0,004
18	6,9	-11	0,36	0,44	0,44	9,66	2,26	1,71	0,004
22	6,8	-11	0,32	0,34	0,34	9,15	2,26	2,53	0,005
24	6,6	23	0,26	0,28	0,28	8,75	1,37	2,02	0,004
28	6,5	56	0,23	0,24	0,24	8,60	1,86	1,70	0,007

Doebern, Oktober 1997

Teufe cm	pH	Eh mV	SRP $\mu\text{mol l}^{-1}$	NH_4^+ mmol l^{-1}	NO_3^- $\mu\text{mol l}^{-1}$	SO_4^{2-} mmol l^{-1}	DOC mmol l^{-1}	Fe mmol l^{-1}	Mn mmol l^{-1}
-5			0,06	0,08	n.b.	8,47	0,09	<0,001	0,027
0	6,4	238	0,03	0,14	n.b.	8,97	1,30	0,03	0,029
1	6,5	209	0,10	0,18	n.b.	10,06	1,53	0,94	0,034
2	6,8	164	0,13	0,24	n.b.	10,52	1,92	1,40	0,031
3	6,9	120	0,19	0,29	n.b.	11,46	3,06	3,08	0,031
4	6,9	106	0,26	0,34	n.b.	14,58	4,23	4,26	0,035
5	7,0	n.b.	0,36	0,40	n.b.	13,02	6,34	5,57	0,032
6	7,1	84	0,39	0,46	n.b.	13,23	5,52	6,98	0,032
7	7,1	65	0,39	0,47	n.b.	13,75	6,16	6,68	0,025
8	7,2	56	0,36	0,47	n.b.	13,96	6,50	6,82	0,023
9	7,1	56	0,36	0,50	n.b.	13,96	6,08	7,03	0,018
10	7,1	55	0,39	0,51	n.b.	14,38	6,46	6,80	0,015
12	7,0	58	0,42	0,51	n.b.	14,27	0,75	7,71	0,011
14	7,0	60	0,45	0,52	n.b.	14,79	0,76	8,57	0,009
16	6,9	74	0,48	0,53	n.b.	15,83	0,72	8,88	0,009
18	6,8	84	0,48	0,50	n.b.	15,94	0,72	8,61	0,010
21	6,6	105	0,45	0,46	n.b.	16,77	0,54	9,24	0,017
24	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	3,72	0,034

Doebern, Mai 1998

Teufe cm	pH	Eh mV	SRP $\mu\text{mol l}^{-1}$	NH_4^+ mmol l^{-1}	NO_3^- $\mu\text{mol l}^{-1}$	SO_4^{2-} mmol l^{-1}	DOC mmol l^{-1}	Fe mmol l^{-1}	Mn mmol l^{-1}
-5			0,42	0,11	20,70	2,71	0,14	0,12	n.b.
1	6,2	209	0,13	0,20	2,50	5,68	4,66	0,98	0,024
2	6,2	162	0,13	0,28	3,21	8,65	3,00	1,42	0,029
3	6,3	119	0,13	n.b.	5,42	9,13	3,33	1,99	0,026
4	6,4	86	0,16	n.b.	3,93	9,52	3,83	2,70	0,026
5	6,5	80	0,26	0,37	3,85	9,01	6,33	2,62	0,025
6	6,5	62	0,32	n.b.	4,21	10,52	6,49	3,55	0,022
7	6,7	35	0,39	0,48	6,07	9,66	5,83	3,18	0,021
8	6,6	25	0,29	0,37	9,28	6,72	6,49	3,80	0,019
9	6,7	14	0,32	0,20	9,28	3,51	8,16	3,10	0,018
10	6,7	15	0,26	0,18	9,28	3,24	6,99	3,67	0,015
11	6,8	-15	0,36	0,54	13,56	9,27	8,33	3,84	0,011
13	6,8	-26	0,39	0,61	4,64	9,39	9,91	3,35	0,009
15	6,8	-30	0,29	0,60	4,71	8,78	7,74	3,06	0,006
17	6,8	-21	0,36	0,59	4,35	8,81	7,24	2,86	0,004
19	6,7	-6	0,26	0,64	7,85	5,42	6,41	2,79	0,003
21	6,7	0	0,29	0,38	14,28	7,85	6,79	2,61	0,002
23	6,7	-15	0,52	0,60	23,55	7,65	5,78	2,60	0,002
25	6,8	4	0,26	0,55	11,42	7,88	5,92	2,70	0,003
27	6,7	4	0,45	0,56	8,57	8,10	4,89	2,74	0,003
29	6,6	32	5	0,32	n.b.	7,14	4,73	0,00	0,005
31	6,6	21	0,29	0,31	7,00	7,73	4,27	2,49	0,008
33	6,6	25	0,26	0,50	18,56	4,42	4,05	1,73	0,012
35	6,5	-37	0,26	0,29	5,50	n.b.	n.b.	0,70	0,015

Porenwasser

Experiment 1, 8 Wochen

Tiefe cm	pH	Eh mV	SRP $\mu\text{mol l}^{-1}$	NH_4^+ mmol l^{-1}	NO_3^- $\mu\text{mol l}^{-1}$	SO_4^{2-} mmol l^{-1}	DOC mmol l^{-1}	Fe mmol l^{-1}	Mn mmol l^{-1}
-1	7.0	n.b.	0.06	0.002	294.85	2.34	0.47	<0.001	n.b.
1	4.3	235	0.13	0.17	3.43	9.08	11.91	0.66	0.019
2	4.6	365	0.31	0.09	15.70	11.46	48.79	2.72	0.028
3	4.8	324	1.68	0.10	3.21	12.40	69.44	3.74	0.037
4	5.0	289	0.43	0.11	14.28	16.46	98.58	5.05	0.045
5	5.1	269	0.34	0.12	<0.42	17.81	100.42	6.16	0.054
6	5.2	n.b.	0.52	0.17	n.b.	21.67	93.09	7.52	0.071
7	5.5	174	n.b.	n.b.	n.b.	23.02	65.28	6.55	0.078
8	5.6	181	n.b.	n.b.	n.b.	24.17	47.13	5.83	0.076
9	5.7	172	n.b.	n.b.	n.b.	26.67	51.29	7.23	0.079
10	5.8	154	n.b.	n.b.	n.b.	n.b.	41.63	7.59	0.073
12	5.9	131	0.38	0.22	n.b.	25.52	36.22	7.57	0.000
13	6.0	127	n.b.	n.b.	n.b.	n.b.	38.05	8.16	0.064
14	6.0	129	0.38	0.18	n.b.	26.15	35.30	7.79	0.069
15	6.0	129	0.45	0.19	n.b.	27.40	33.14	7.45	0.072
16	6.1	116	0.51	0.28	n.b.	25.73	33.72	7.12	0.069

Experiment 1, 16 Wochen

Tiefe cm	pH	Eh mV	SRP $\mu\text{mol l}^{-1}$	NH_4^+ mmol l^{-1}	NO_3^- $\mu\text{mol l}^{-1}$	SO_4^{2-} mmol l^{-1}	DOC mmol l^{-1}	Fe mmol l^{-1}	Mn mmol l^{-1}
-1	7.0	n.b.	0.05	0.002	2.93	3.30	0.79	4.53	n.b.
1	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.
2	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.
3	4.2	369	1.68	0.31	1.78	32.19	2.03	27.03	0.022
4	4.8	310	2.26	0.39	1.71	42.40	4.18	37.77	0.031
5	5.1	272	3.23	0.55	0.86	55.94	3.90	48.86	0.039
6	5.3	252	3.55	0.61	0.93	61.56	5.45	62.82	0.053
7	5.3	253	3.87	0.71	1.21	72.60	5.67	63.36	0.050
8	5.3	225	4.20	0.77	1.86	73.33	7.17	65.33	0.051
9	5.4	228	4.52	0.86	3.64	80.83	8.70	69.45	0.053
10	5.4	218	4.84	0.96	1.64	86.67	9.39	75.71	0.058
11	5.4	195	5.17	1.08	2.00	97.60	11.77	78.93	0.058
13	5.4	216	5.17	1.18	1.93	98.29	14.18	78.93	0.057
15	5.4	201	5.17	1.26	1.43	95.94	12.32	81.87	0.060
17	5.3	204	5.49	1.40	1.14	89.48	13.85	77.68	0.056
19	5.2	206	4.84	1.16	1.50	88.75	11.05	76.25	0.055
21	5.1	216	4.84	1.25	2.78	86.98	11.54	75.17	0.057
23	5.1	213	4.84	1.25	1.00	87.81	11.10	75.00	0.055
25	5.0	211	4.84	1.32	1.28	88.85	10.56	77.68	0.059
27	5.0	220	4.84	1.27	9.99	87.19	10.10	74.28	0.056
29	4.8	219	4.52	1.07	1.78	83.96	10.84	75.71	0.058
31	4.8	225	4.84	1.10	2.57	85.00	10.71	77.20	0.061
33	4.7	255	4.84	1.12	2.07	82.92	10.07	77.14	0.062
35	4.8	253	4.52	1.18	15.70	73.75	9.34	72.67	0.058
37	4.9	229	4.20	1.01	3.85	75.94	8.68	67.12	0.055

Experiment 1, 24 Wochen

Tiefe cm	pH	Eh mV	SRP $\mu\text{mol l}^{-1}$	NH_4^+ mmol l^{-1}	NO_3^- $\mu\text{mol l}^{-1}$	SO_4^{2-} mmol l^{-1}	DOC mmol l^{-1}	Fe mmol l^{-1}	Mn mmol l^{-1}
-1	7.0	n.b.	0.0969	0.0014	3.57	1.67	0.87	0.001	n.b.
1	5.6	204	0.71	0.18	7.85	7.72	1.90	5.78	0.007
2	6.1	113	0.52	0.26	7.14	6.24	4.46	7.86	0.008
3	6.3	83	0.74	0.33	1.14	10.39	5.48	10.26	0.011
4	6.3	86	0.77	0.36	7.14	11.77	6.84	11.58	0.011
5	6.1	105	0.81	0.42	9.28	12.40	6.48	13.10	0.013
6	5.5	135	0.84	0.44	11.42	15.00	6.29	14.27	0.015
7	5.4	211	0.87	0.58	n.b.	16.04	5.20	13.60	0.018
8	4.7	298	1.03	0.75	15.70	23.75	2.73	20.23	0.025
9	4.6	304	1.07	0.77	12.85	24.17	2.63	18.61	0.026
10	4.7	290	1.16	0.84	14.28	26.04	2.22	21.12	0.027
11	4.8	275	1.16	0.87	9.28	26.88	2.51	21.48	0.028
12	5.0	259	1.13	0.90	7.07	26.98	2.03	21.66	0.029
13	5.0	269	1.19	0.87	9.99	26.98	2.63	21.66	0.028
14	4.9	266	1.29	0.95	10.71	28.23	2.06	22.91	0.030
15	4.7	286	1.23	0.97	3.35	26.67	1.47	22.19	0.030

Porenwasser

Experiment 2, 8 Wochen

Teufe	pH	Eh	SRP	NH ₄ ⁺	NO ₃ ⁻	SO ₄ ²⁻	DOC	Fe	Mn
cm		mV	$\mu\text{mol l}^{-1}$	mmol l^{-1}	$\mu\text{mol l}^{-1}$	mmol l^{-1}	mmol l^{-1}	mmol l^{-1}	mmol l^{-1}
-1	n.b.	n.b.	0,1	<0,01	376,2	2,82	0,4	<0,01	
1	5,5	135	8,69	0,2	0,16	38,13	4,08	29,35	0,078
2	5,3	174	9,33	0,21	0,16	49,79	4,83	36,69	0,087
4	4,8	260	0,96	0,14	0,19	59,48	4,08	44,03	0,106
5	4,9	253	0,93	0,10	0,44	63,44	4,25	50,12	0,120
6	5,3	198	1,02	0,14	0,24	66,25	8,58	49,58	0,127
7	5,4	181	1,00	0,08	0,24	66,04	9,99	33,52	0,142
8	5,5	175	0,94	0,10	0,29	62,40	11,82	48,51	0,131
9	5,4	170	0,94	0,09	0,19	56,98	13,07	50,65	0,141
10	5,4	182	1,06	0,10	0,23	57,81	13,99	48,68	0,137
11	5,0	227	0,97	0,10	0,50	63,23	13,91	51,01	0,144
13	4,7	266	1,24	0,06	0,27	66,88	16,37	52,80	0,151
15	4,8	253	1,00	0,06	0,23	60,83	8,83	51,73	0,143
17	4,5	289	0,98	0,04	0,27	65,21	5,50	56,38	0,156
19	4,4	313	0,98	0,10	0,27	61,56	4,66	51,91	0,145
21	4,4	312	0,99	0,05	0,37	67,60	4,75	52,26	0,148
23	4,4	304	1,00	0,09	0,32	58,34	4,00	54,59	0,155
25	4,7	333	0,93	0,04	0,31	61,64	3,41	50,30	0,144
27	4,0	355	0,93	0,07	0,48	42,92	3,75	46,89	0,135
29	3,9	338	0,83	0,07	0,55	46,88	4,58	46,00	0,132
31	3,7	378	0,77	0,09	0,48	51,77	4,58	45,64	0,135

Experiment 2, 16 Wochen

Teufe	pH	Eh	SRP	NH ₄ ⁺	NO ₃ ⁻	SO ₄ ²⁻	DOC	Fe	Mn
cm		mV	$\mu\text{mol l}^{-1}$	mmol l^{-1}	$\mu\text{mol l}^{-1}$	mmol l^{-1}	mmol l^{-1}	mmol l^{-1}	mmol l^{-1}
-1	7,0	n.b.	0,03	0,03	21,42	3,40	0,93	<0,01	
1	6,5	29	1,29	0,74	1,78	19,79	25,17	18,26	0,032
2	6,4	59	1,43	0,78	7,85	23,44	31,22	24,34	0,041
3	6,3	69	1,71	0,95	2,57	31,15	37,90	28,82	0,050
4	6,3	59	1,55	0,81	2,14	28,23	36,64	26,31	0,045
5	6,3	54	1,58	0,81	4,21	27,71	35,47	26,31	0,046
6	6,3	52	2,13	1,16	2,86	38,75	37,06	36,16	0,064
7	6,3	61	2,20	1,16	6,14	39,27	35,17	36,16	0,067
8	6,2	58	1,97	1,10	3,00	40,21	28,99	39,74	0,074
9	6,2	78	2,23	1,17	6,78	39,79	30,89	36,33	0,067
10	6,2	84	2,52	1,25	7,85	41,46	37,96	35,44	0,067
11	6,1	104	2,42	1,29	3,43	38,44	23,71	37,23	0,072
12	6,0	119	2,36	1,13	3,64	37,92	24,23	35,44	0,066
13	5,8	141	2,58	n.b.	6,71	50,21	19,14	20,94	0,041
14	5,7	159	2,68	1,40	178,44	52,50	20,61	41,70	0,080

Experiment 2, 24 Wochen

Teufe	pH	Eh	SRP	NH ₄ ⁺	NO ₃ ⁻	SO ₄ ²⁻	DOC	Fe	Mn
cm		mV	$\mu\text{mol l}^{-1}$	mmol l^{-1}	$\mu\text{mol l}^{-1}$	mmol l^{-1}	mmol l^{-1}	mmol l^{-1}	mmol l^{-1}
-1	7,0	n.b.	0,10	0,002	23,56	2,47	0,87	<0,01	
1	6,7	48	1,10	0,52	6,07	16,77	3,33	14,57	0,018
2	6,1	48	2,10	0,83	9,28	27,50	2,86	24,88	0,027
3	6,1	57	1,87	0,94	19,99	34,58	5,03	31,68	0,033
4	5,8	100	1,97	1,05	14,28	39,17	5,00	35,80	0,037
5	5,3	185	2,45	1,09	13,56	45,83	3,95	40,09	0,043
6	4,3	300	2,36	1,11	3,57	48,23	4,22	42,24	0,049
7	3,9	373	2,39	1,13	12,13	51,56	2,24	45,82	0,053
8	3,6	411	2,42	1,17	6,42	55,42	1,92	49,76	0,060
9	3,5	432	2,49	1,16	4,21	58,34	2,56	45,82	0,063
10	3,4	443	2,62	1,16	4,50	59,58	2,77	51,91	0,066
11	3,3	454	2,71	1,14	2,64	62,29	3,26	49,04	0,070
13	3,3	452	2,62	1,15	4,50	63,33	3,88	52,80	0,072
15	3,4	444	2,74	1,18	5,21	67,40	3,54	56,20	0,078
17	3,7	484	2,71	1,09	2,93	65,63	4,15	51,37	0,076
19	3,9	342	2,97	1,15	2,93	69,38	3,93	57,63	0,080
21	4,4	294	2,65	1,04	7,14	63,44	6,36	51,37	0,067

Porenwasser

Experiment 3, 8 Wochen

Tiefe cm	pH	Eh mV	SRP $\mu\text{mol l}^{-1}$	NH_4^+ mmol l^{-1}	NO_3^- $\mu\text{mol l}^{-1}$	SO_4^{2-} mmol l^{-1}	DOC mmol l^{-1}	Fe mmol l^{-1}	Mn mmol l^{-1}
-1	3.0	n.b.	0.23	0.09	274.1	2.52	0.54	0.19	n.b.
1	4.5	249	95.3	0.67	n.b.	18.23	2.16	10.29	0.014
2	5.3	166	62.64	0.77	n.b.	24.17	3.25	13.44	0.020
3	5.4	150	15.92	1.07	n.b.	30.52	3.75	19.15	0.031
4	5.2	204	0.77	0.62	n.b.	34.38	3.91	16.74	0.043
5	4.4	306	0.55	0.78	n.b.	36.25	1.00	25.77	0.045
6	4.2	342	0.53	0.51	n.b.	41.67	1.25	29.35	0.055
7	4.2	344	0.55	0.76	n.b.	43.54	1.50	27.39	0.055
8	4.1	361	0.61	0.59	n.b.	43.33	2.41	30.25	0.066
9	3.9	383	0.55	0.50	n.b.	41.46	1.75	30.61	0.070
10	3.7	403	0.58	0.56	n.b.	43.33	1.67	22.19	0.071

Experiment 3, 16 Wochen

Tiefe cm	pH	Eh mV	SRP $\mu\text{mol l}^{-1}$	NH_4^+ mmol l^{-1}	NO_3^- $\mu\text{mol l}^{-1}$	SO_4^{2-} mmol l^{-1}	DOC mmol l^{-1}	Fe mmol l^{-1}	Mn mmol l^{-1}
-1	3.0	n.b.	0.18	0.20	129.22	3.51	1.16	0.20	n.b.
1	5.6	152	41.98	0.86	2.92	24.17	6.05	19.87	0.034
2	6.0	109	3.22	1.27	1.78	32.60	8.07	n.b.	n.b.
3	6.1	115	4.84	1.19	2.86	39.69	7.69	34.54	0.066
4	6.0	114	5.17	1.36	4.07	42.92	9.53	37.23	0.072
5	5.9	127	3.55	1.43	1.93	45.52	9.34	39.56	0.079
6	5.7	165	3.04	1.42	2.36	49.48	8.28	41.88	0.089
7	5.3	221	3.55	1.83	2.14	61.46	6.35	50.12	0.107
8	4.9	272	3.87	1.98	6.35	67.50	4.39	55.49	0.121
9	4.8	275	3.87	1.78	2.86	67.60	4.35	54.41	0.123
10	4.8	279	3.55	1.77	2.00	64.90	4.20	51.37	0.120
11	4.6	304	3.55	1.69	2.57	67.40	3.98	53.70	0.126
13	4.4	327	3.55	1.80	2.36	64.48	3.52	53.31	0.133
15	4.3	339	3.87	1.84	2.78	70.10	3.71	55.49	0.137
17	4.2	350	3.55	1.90	2.71	69.79	3.36	54.77	0.135
19	4.0	368	3.16	1.65	2.21	70.63	3.16	54.59	0.137

Experiment 3, 24 Wochen

Tiefe cm	pH	Eh mV	SRP $\mu\text{mol l}^{-1}$	NH_4^+ mmol l^{-1}	NO_3^- $\mu\text{mol l}^{-1}$	SO_4^{2-} mmol l^{-1}	DOC mmol l^{-1}	Fe mmol l^{-1}	Mn mmol l^{-1}
-1	7.0	n.b.	0.10	<0.01	54.2586	2.23	0.92	<0.01	n.b.
1	6.2	37	2.45	0.85	5.21	21.88	3.56	19.15	0.024
2	6.0	66	2.74	1.09	3.71	31.46	4.85	23.81	0.035
3	5.9	93	1.74	1.09	3.00	32.50	5.30	24.70	0.041
4	5.6	143	1.91	1.23	4.50	44.17	5.35	37.59	0.050
5	5.1	189	2.74	1.16	7.14	44.58	4.82	36.16	0.050
6	4.6	275	2.23	1.26	2.36	52.08	3.66	43.31	0.058
7	4.1	343	2.23	1.22	3.43	52.19	3.02	45.10	0.064
8	3.9	369	2.42	1.32	6.64	58.54	2.29	44.03	0.073
9	3.8	390	2.42	1.26	4.93	57.81	2.47	48.15	0.074
10	3.7	401	2.49	1.26	5.92	58.44	2.86	48.15	0.077
11	3.6	418	2.68	1.26	5.21	61.25	2.96	51.01	0.086
13	3.5	426	2.45	1.15	3.00	57.40	4.65	42.24	0.073
15	3.5	425	2.42	1.13	4.43	60.10	2.71	46.89	0.083
17	3.6	425	2.45	1.13	3.35	58.54	3.35	47.97	0.088
19	3.6	420	2.39	1.08	4.64	57.29	4.81	48.86	0.089
21	3.6	404	2.26	0.99	1.36	53.54	5.73	41.17	0.082
23	3.7	382	2.29	0.96	1.57	53.85	4.80	44.21	0.082
25	3.9	351	2.23	0.95	2.21	53.85	5.41	43.67	0.082
27	4.3	301	1.94	0.80	n.b.	45.31	8.99	26.49	0.073

Umlaufwasser der Experimente

Tage	Experiment 1				Experiment 2				Experiment 3			
	SRP	Fe	SO ₄ ²⁻	NH ₄ ⁺	SRP	Fe	SO ₄ ²⁻	NH ₄ ⁺	SRP	Fe	SO ₄ ²⁻	NH ₄ ⁺
	μmol l ⁻¹	μmol l ⁻¹	mmol l ⁻¹	μmol l ⁻¹	μmol l ⁻¹	μmol l ⁻¹	mmol l ⁻¹	μmol l ⁻¹	μmol l ⁻¹	μmol l ⁻¹	mmol l ⁻¹	μmol l ⁻¹
5	<0,1	7,66	1,24	34,98	232,5	0,86	1,41	37,12	242,2	5,17	1,31	43,54
7	0,26	13,09	1,43	n.b.	216,3	1,11	1,48	34,98	238,9	1,25	1,49	68,52
8	0,32	4,23	1,33	52,11	11,3	2,72	1,30	128,48	32,3	5,01	1,23	67,09
10	<0,1	8,09	0,11	33,55	11,0	3,17	1,37	32,83	125,9	4,48	1,29	178,44
12	<0,1	32,23	1,53	25,70	8,72	6,34	1,42	26,41	184,0	4,92	1,32	85,65
13	<0,1	6,39	1,63	12,13	1,58	6,37	1,33	17,13	216,3	6,20	1,44	78,52
14	1,07	4,60	1,25	21,41	2,32	4,53	1,25	20,70	12,6	1,54	1,22	37,12
17	<0,1	7,29	1,36	16,42	0,45	3,87	1,36	38,54	32,3	5,41	1,33	49,25
19	<0,1	4,69	1,46	26,41	0,26	2,44	1,53	49,96	42,0	14,32	1,45	71,38
21	<0,1	4,96	1,49	18,56	0,13	2,47	1,50	37,83	45,2	22,92	1,45	61,38
22	0,71	6,32	1,42	30,69	n.b.	n.b.	n.b.	0,00	n.b.	n.b.	n.b.	n.b.
24	<0,1	3,53	1,50	21,41	0,13	2,44	1,62	52,11	54,9	67,50	1,61	92,79
26	<0,1	3,33	1,51	32,83	0,10	1,77	1,70	36,40	58,1	102,78	1,66	107,07
30	0,94	n.b.	1,65	9,28	0,05	n.b.	1,86	20,70	22,0	n.b.	1,84	64,24
34	0,65	n.b.	1,81	5,14	<0,06	n.b.	2,02	4,28	22,8	n.b.	2,00	92,08
37	2,87	1,06	2,00	5,57	0,12	0,48	2,20	1,86	32,3	334,83	2,20	117,06
41	0,23	1,32	1,98	9,28	0,13	0,59	2,23	11,42	12,9	368,85	2,23	126,34
44	<0,06	0,38	2,12	4,57	<0,06	2,94	2,44	13,13	3,26	n.b.	2,46	107,07
48	0,06	0,93	1,96	27,91	0,06	0,68	2,35	7,85	1,65	404,66	2,52	137,76
56	0,06	0,79	2,34	<1,43	0,05	0,47	2,82	<1,43	0,23	193,38	2,52	88,51
59	<0,06	2,72	2,40	11,71	<0,06	1,83	2,24	8,85	1,99	115,67	3,49	28,77
62	0,26	3,31	3,33	7,57	<0,06	42,26	4,34	<1,43	0,71	120,14	3,78	94,22
65	0,89	1,86	1,85	1,64	0,24	10,80	1,72	1,43	1,68	158,64	1,40	44,90
69	<0,06	35,27	0,80	<2,14	0,24	36,53	1,72	1,43	1,70	269,65	1,40	44,90
72	<0,06	3,65	2,70	8,71	<0,06	1,58	1,11	8,99	1,59	335,18	2,08	76,37
76	n.b.	1,16	0,00	0,00	<0,06	3,21	1,71	10,99	1,55	252,46	2,41	98,00
80	<0,06	1,86	2,91	6,64	0,06	2,51	1,97	6,85	1,23	225,60	2,85	102,78
83	0,08	3,01	2,98	9,56	<0,06	3,22	3,01	12,06	0,77	383,17	3,26	112,78
90	<0,06	5,55	0,00	4,43	<0,06	8,59	2,00	18,34	0,11	354,52	2,71	139,26
98	<0,06	8,25	3,68	7,35	<0,06	5,09	2,43	17,70	0,05	254,25	3,57	160,60
105	0,68	7,61	5,44	2,78	n.b.	5,62	4,12	20,70	0,48	347,36	4,82	190,58
112	<0,06	4,53	3,30	<1,43	<0,06	1,31	3,41	34,19	0,18	202,33	3,51	203,43
120	0,06	8,77	1,21	4,14	<0,06	32,05	1,35	22,13	<0,06	6,34	1,32	19,99
122	<0,06	10,24	1,21	3,35	<0,06	41,90	1,41	24,27	<0,06	8,88	1,37	14,28
126	<0,06	23,10	1,25	2,14	<0,06	158,46	1,56	36,40	<0,06	62,67	1,47	21,41
128	<0,06	17,73	1,28	7,14	<0,06	204,12	1,69	51,39	<0,06	95,43	1,57	30,69
133	<0,06	21,31	1,30	3,78	<0,06	263,21	1,83	50,68	0,06	139,84	1,69	34,26
136	<0,06	32,23	1,35	1,43	<0,06	225,60	1,90	49,25	<0,06	165,98	1,78	42,83
140	<0,06	41,36	1,41	8,57	0,10	359,89	2,11	57,10	<0,06	200,54	1,83	52,82
142	<0,06	2,17	1,37	4,93	<0,06	<0,36	2,09	46,40	0,10	1,32	1,84	51,39
147	0,03	2,90	1,46	n.b.	<0,06	0,39	2,10	0,00	<0,06	2,72	1,91	0,00
150	0,06	4,83	1,47	3,85	<0,06	<0,36	2,20	23,55	0,06	0,57	2,04	18,56
154	0,06	3,06	1,51	3,28	0,06	<0,36	2,25	5,64	<0,06	0,72	1,76	2,71
161	0,06	1,25	1,61	<1,43	0,06	0,43	2,34	1,64	<0,06	0,47	2,01	1,71
168	<0,1	n.b.	1,67	<1,43	<0,1	0,86	2,47	1,57	<0,10	1,38	2,23	<1,43

Zu allen Zeitpunkten, die unterstrichen sind, mußte das Umlaufwasser gewechselt werden.

Sediment

Niemegk, April 1997

Sedimenttiefe	DW	Na	Mg	Al	Si	P	K	Ca	Mn	Fe	Ni	Zn	As
cm	%	mg g ⁻¹	mg g ⁻¹	mg g ⁻¹	mg g ⁻¹	µg g ⁻¹	mg g ⁻¹	mg g ⁻¹	µg g ⁻¹	mg g ⁻¹	µg g ⁻¹	µg g ⁻¹	µg g ⁻¹
1	3,7	0,74	1,15	22,6	63,1	462,8	4,38	3,10	46,0	297,3	n.b.	n.b.	n.b.
2	2,8	0,94	0,68	25,5	68,0	323,9	5,04	1,86	30,7	300,1	5,54	10,68	133,3
3	4,1	n.b.	n.b.	24,9	73,4	262,0	5,25	1,86	30,0	297,5	n.b.	n.b.	128,0
4	4,1	n.b.	n.b.	25,6	74,0	349,3	5,16	1,86	32,0	295,4	n.b.	n.b.	137,0
5	5,0	n.b.	n.b.	26,3	79,2	327,5	5,35	1,79	31,0	275,4	n.b.	n.b.	129,0
6	5,8	n.b.	n.b.	25,2	78,2	371,1	5,25	1,93	33,0	279,3	n.b.	n.b.	133,0
7	5,8	n.b.	n.b.	25,1	81,5	320,5	5,46	2,07	32,0	272,6	n.b.	n.b.	127,0
8	6,4	n.b.	n.b.	25,4	77,8	362,4	5,18	1,86	31,0	284,7	n.b.	n.b.	128,0
9	6,7	n.b.	n.b.	25,0	73,6	361,5	5,28	1,86	32,0	292,1	n.b.	n.b.	133,0
10	6,4	0,30	0,60	22,7	65,4	349,3	4,45	1,57	31,0	296,1	6,0	13,0	120,0
11	6,9	0,30	0,66	22,4	65,3	362,8	4,43	1,64	30,0	295,8	4,0	10,0	125,0
13	6,8	0,30	0,72	26,9	79,1	373,3	4,91	1,64	30,0	287,3	5,0	13,0	119,0
15	7,4	0,37	1,09	38,6	110,1	316,5	6,90	1,43	32,0	249,8	5,0	14,0	106,0
17	9,0	0,52	1,57	52,0	162,8	255,0	10,33	1,29	46,0	191,0	9,0	18,0	100,0
19	10,9	0,59	1,75	51,9	163,1	247,1	11,01	1,43	58,0	184,4	8,0	18,0	99,0
21	10,7	0,52	1,69	46,4	144,0	304,8	9,51	1,21	56,0	223,5	11,0	22,0	109,0
23	12,0	0,37	1,45	43,6	133,3	262,0	7,73	1,00	34,0	238,4	8,0	20,0	100,0
25	15,9	0,67	1,81	38,9	244,6	158,9	10,33	1,43	34,0	86,9	10,0	20,0	110,0

Niemegk, Oktober 1997

Sedimenttiefe	DW	Na	Mg	Al	Si	P	K	Ca	Mn	Fe
cm	%	mg g ⁻¹	mg g ⁻¹	mg g ⁻¹	mg g ⁻¹	mg g ⁻¹	mg g ⁻¹	mg g ⁻¹	µg g ⁻¹	mg g ⁻¹
1	3,3	0,55	0,90	25,5	50,9	620,4	5,45	2,56	40,0	311,3
2	6,9	0,54	1,40	37,2	94,6	625,1	8,52	2,95	60,0	226,8
3	8,1	0,60	1,53	42,8	110,3	601,9	9,63	3,08	60,0	204,2
4	9,4	0,53	1,34	34,2	109,3	518,6	7,98	3,68	82,0	225,6
5	10,5	0,47	1,06	24,2	134,6	407,4	6,03	3,66	70,0	193,1
6	11,3	0,65	1,52	41,5	127,5	560,2	9,62	3,37	84,0	190,7
7	11,6	0,53	1,45	36,1	115,3	1014,0	7,96	3,67	85,0	202,6
8	12,6	0,48	1,25	37,9	135,9	666,7	8,98	2,20	53,0	219,2
9	18,7	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.
10	24,8	0,45	0,92	26,3	245,0	189,8	7,28	2,81	25,0	75,8
11	11,7	0,49	1,38	36,9	96,7	638,9	7,18	2,70	60,0	233,4
13	11,8	0,36	0,93	25,7	74,7	495,4	5,18	2,03	45,0	300,9
15	7,4	0,32	0,54	7,7	15,7	481,5	1,33	2,31	68,0	404,0
17	9,0	0,61	1,31	27,2	86,2	393,6	8,95	2,86	52,0	256,2
19	9,7	0,55	0,87	23,5	44,6	657,5	4,47	1,98	51,0	321,1
22	14,4	0,72	1,85	65,2	147,9	291,7	14,00	1,66	50,0	140,4
26	15,3	0,48	1,60	46,7	99,3	449,1	10,33	1,69	60,0	247,7
29	19,8	0,48	1,30	41,9	120,3	347,3	8,78	1,75	52,0	207,3
32	44,7	0,60	1,31	39,0	261,1	115,8	13,84	1,52	60,0	42,7

Niemegk, Mai 1998

Sedimenttiefe	DW	Na	Mg	Al	Si	P	K	Ca	Mn	Fe
cm	%	mg g ⁻¹	mg g ⁻¹	mg g ⁻¹	mg g ⁻¹	µg g ⁻¹	mg g ⁻¹	mg g ⁻¹	µg g ⁻¹	mg g ⁻¹
4	3,2	0,42	0,91	14,4	44,8	820,8	2,94	2,13	53,0	350,0
5	3,2	0,44	0,98	14,2	42,8	663,7	2,71	2,17	38,0	357,3
7	4,1	0,43	1,01	18,2	49,6	641,8	3,45	2,09	35,0	349,3
9	4,0	0,47	1,09	21,7	69,5	637,5	4,47	1,95	45,0	323,5
11	6,1	0,50	1,36	32,4	99,1	668,0	6,28	2,03	46,0	276,3
15	7,8	0,50	1,45	44,2	104,5	995,5	6,59	2,42	69,0	274,4
17	10,5	0,55	1,11	31,7	247,7	318,7	9,88	1,35	45,0	181,6
21	13,9	0,51	0,95	27,2	325,5	262,0	8,63	1,11	53,0	125,8
25	11,2	0,44	1,24	38,4	94,7	654,9	6,72	1,55	50,0	289,1
35	9,8	0,75	1,50	54,5	202,1	318,7	14,28	1,45	60,0	169,1

Sediment

Doebern, April 1997

Sedimenttiefe cm	DW %	Na mg g ⁻¹	Mg mg g ⁻¹	Al mg g ⁻¹	Si mg g ⁻¹	P µg g ⁻¹	K mg g ⁻¹	Ca mg g ⁻¹	Mn µg g ⁻¹	Fe mg g ⁻¹	Ni µg g ⁻¹	Zn µg g ⁻¹	As µg g ⁻¹
1	4,6	0,37	0,12	26,2	83,1	388,6	2,69	9,35	220,0	333,7	0,0	64,0	11,0
2	8,7	0,30	1,21	41,5	134,2	426,6	4,74	10,93	233,0	243,7	111,9	83,0	13,0
3	6,5	0,15	0,72	31,2	96,4	341,9	2,98	9,22	129,0	314,9	76,9	55,0	7,0
4	5,4	0,22	0,66	20,6	79,7	458,5	1,78	10,08	92,0	362,6	56,0	49,0	7,0
5	7,4	0,22	0,66	30,8	94,3	394,3	2,91	9,08	71,0	298,8	35,0	51,0	6,0
6	6,6	0,15	0,72	29,3	99,9	332,7	2,66	8,79	83,0	334,4	69,9	78,0	9,0
7	6,5	0,22	0,66	33,1	98,1	425,7	2,44	7,65	78,0	328,5	56,0	69,0	9,0
8	5,9	0,15	0,60	21,9	67,5	397,3	1,49	6,15	72,0	391,5	42,0	40,0	10,0
9	6,1	0,15	0,48	27,1	83,0	481,2	1,82	6,15	56,0	378,6	28,0	39,0	11,0
10	7,3	0,15	0,54	31,1	90,3	395,6	2,47	6,22	55,0	345,8	35,0	50,0	12,0
11	7,7	0,15	0,48	31,1	83,6	341,0	2,01	6,36	67,0	346,0	49,0	77,0	9,0
13	8,4	0,30	0,90	51,0	158,0	957,9	4,76	5,79	130,0	236,3	153,9	127,0	10,0
14	8,3	0,30	0,84	46,5	153,1	1143,9	4,05	6,36	215,0	258,3	125,9	97,0	15,0
15	8,9	0,22	0,60	38,1	112,1	608,2	3,08	6,43	177,0	317,1	62,9	81,0	14,0
16	10,7	0,22	0,78	45,5	121,4	361,1	3,55	6,65	146,0	286,0	90,9	99,0	16,0
18	10,7	0,30	1,21	65,9	170,0	466,7	4,98	5,50	161,0	236,6	139,9	98,0	17,0
20	12,6	0,30	1,21	61,1	154,0	498,6	4,59	5,93	254,0	235,1	146,9	145,0	25,0
22	11,3	0,22	0,90	50,7	145,6	482,0	3,96	5,72	90,0	266,2	160,9	295,0	27,0
24	9,2	0,30	1,09	60,7	156,2	275,1	4,45	5,86	70,0	228,1	139,9	192,0	29,0
25	9,7	0,37	1,33	76,5	175,6	337,1	5,26	6,50	70,0	162,1	132,9	140,0	20,0

Doebern, Oktober 1997

Sedimenttiefe cm	DW %	Na mg g ⁻¹	Mg mg g ⁻¹	Al mg g ⁻¹	Si mg g ⁻¹	P µg g ⁻¹	K mg g ⁻¹	Ca mg g ⁻¹	Mn µg g ⁻¹	Fe mg g ⁻¹
1	3,7	0,35	0,76	29,9	64,9	444,5	3,04	11,26	205,0	345,1
2	2,8	0,28	0,74	24,7	55,8	328,7	2,47	12,45	160,0	353,4
3	4,1	1,12	1,30	41,8	82,5	463,0	4,24	12,06	146,0	296,8
4	4,1	0,43	0,83	35,1	80,5	597,3	3,28	10,85	123,0	315,7
5	5,0	0,33	1,05	40,8	100,8	546,3	5,93	10,88	130,0	243,5
6	5,8	0,32	0,58	25,3	64,5	578,8	2,58	8,31	123,0	382,8
7	5,8	0,26	0,61	29,3	62,1	634,3	2,29	7,23	110,0	360,4
8	6,4	0,27	0,18	16,2	37,6	606,5	0,84	5,87	100,0	445,3
9	6,7	0,40	0,48	31,5	65,9	754,7	2,46	6,50	85,0	367,6
10	6,4	0,23	0,48	27,0	56,6	439,9	1,89	6,68	78,0	376,2
11	6,9	0,24	0,66	37,2	71,8	615,8	2,71	7,85	105,0	319,3
13	6,8	0,51	0,94	50,9	107,5	1347,3	3,96	7,36	177,0	279,0
15	7,4	0,25	0,79	48,5	89,4	504,7	3,82	8,76	169,0	288,7
17	9,0	0,35	1,12	64,1	120,8	665,2	5,03	7,78	170,0	239,4
19	10,9	0,84	1,13	57,5	110,5	713,0	4,61	8,46	246,0	252,5
23	10,7	0,42	1,18	63,2	118,8	412,1	4,86	7,82	60,0	219,9
26	12,0	0,04	0,15	4,8	397,6	32,4	0,65	3,37	0,0	6,7

Sediment

Niemegk, April 1997

Teufe cm	C mg g ⁻¹	N mg g ⁻¹	S mg g ⁻¹
1	47,4	1,5	48,6
2	48,2	1,5	45,9
3	48,9	1,4	45,6
4	50,3	1,4	45,8
5	54,7	1,5	44,7
6	55,3	1,5	44,6
7	58,6	1,8	46,6
8	55,2	2,3	47,4
9	59,5	2,5	53,9
10	48,8	1,9	48,8
11	49,1	2,0	48,3
13	52,3	2,2	46,6
15	59,0	1,7	42,2
17	72,2	1,6	30,8
19	74,7	1,6	32,7
21	73,3	1,9	32,8
23	91,7	1,9	24,5
25	154,0	2,1	28,8

Doebern, April 1997

Teufe cm	C mg g ⁻¹	N mg g ⁻¹	S mg g ⁻¹
1	57,0	2,1	6,5
2	65,0	2,3	6,7
3	73,0	2,7	6,3
4	99,0	2,6	20,7
5	113,0	2,5	8,3
6	54,0	1,7	5,5
7	53,0	2,1	5,3
8	33,0	1,3	4,3
9	46,0	1,6	4,7
10	51,0	1,8	5,1
11	70,0	2,5	6,2
13	55,0	2,3	11,3
15	80,0	2,1	6,4
17	66,0	1,6	5,1
19	71,0	2,1	7,2

Experiment 1, 24 Wochen

Teufe cm	C mg g ⁻¹	Corg mg g ⁻¹	N mg g ⁻¹	S mg g ⁻¹
1	72,3	70,1	1,8	18,7
2	77,3	74,3	2,1	13,5
3	82,8	81,2	2,4	12,4
4	88,5	86,3	2,6	12,2
5	87,1	86,0	2,6	12,5
6	97,7	94,8	2,0	12,1
7	156	n.b.	1,7	12,5
8	101	n.b.	1,3	9,6
9	115	115	1,6	11
10	97,8	102,0	1,4	12,1
11	84,7	82,0	1,4	12,2
12	63,0	65,6	1,2	9,6
13	117	116	2,2	15,4
14	69,2	71,9	1,6	15,3
15	68,9	68,4	1,4	16,4

Experiment 2, 24 Wochen

Teufe cm	C mg g ⁻¹	Corg mg g ⁻¹	N mg g ⁻¹	S mg g ⁻¹
1	57,0	56,4	8,2	25,4
2	41,2	42,9	4,7	18,2
3	55,5	54,2	2,1	11,4
4	72,0	71,8	2,9	17,0
5	76,9	76,7	3,3	19,5
6	66,1	67,0	2,9	22,3
7	72,9	73,9	1,9	21,4
8	70,7	72,8	1,6	24,1
9	67,0	66,5	2,3	31,2
10	57,2	58,0	2,0	31,6
11	48,2	47,5	1,6	34,2
13	49,9	48,2	2,0	32,3
15	74,3	75,4	1,6	24,2
17	70,3	69,4	1,7	24,3
19	73,3	72,3	1,9	20,1
21	149	149,0	2,0	21,0

Experiment 3, 24 Wochen

Teufe cm	C mg g ⁻¹	Corg mg g ⁻¹	N mg g ⁻¹	S mg g ⁻¹
1	44,3	46,3	7,1	23,5
2	36,7	35,7	2,5	12,5
3	65,7	63,2	1,8	14,4
4	87,0	85,8	3,0	22,6
5	78,2	77,8	3,3	21,0
6	74,2	71,8	3,7	19,6
7	89,4	88,8	1,8	19,9
8	92,4	87,3	n.b.	18,7
9	76,0	77,4	1,8	23,8
10	78,0	78,0	3,0	32,1
11	54,8	55,1	1,8	29,6
13	62,0	61,1	1,9	37,0
15	64,9	64,8	2,1	31,3
17	82,1	82,9	1,6	22,0
19	84,8	83,8	1,7	21,8
21	71,5	70,4	1,7	22,9
23	74,5	74,1	2,0	24,4
25	97,0	97,1	1,7	18,9
27	112	112,3	1,5	18,4

P-Extraktion

Niemegk, Mai 1998

Sedimenttiefe cm	Pges mg g ⁻¹	TP-NH ₄ Cl %	TP-BD %	TP-NaOH %	TP-HCL %	TP-Residual %
1	0,63	2,1	71,4	22,0	2,2	2,4
3	0,74	1,5	73,8	22,1	2,1	0,5
5	0,74	3,7	64,4	20,0	10,2	1,7
7	0,53	1,5	77,1	18,6	1,7	1,1
9	0,64	1,8	75,8	18,2	1,7	2,5
11	0,55	1,1	58,5	35,7	1,4	3,3
13	0,69	0,7	24,2	72,0	0,9	2,2
15	0,79	0,5	18,0	77,2	3,2	1,0
17	0,35	0,7	35,6	60,1	0,7	2,9
19	0,37	0,5	27,9	69,7	0,4	1,5
21	0,26	0,8	59,1	36,9	0,9	2,3
23	0,41	0,9	42,2	53,5	1,1	2,4
25	0,62	0,4	16,1	82,1	0,5	0,9
27	0,40	0,7	13,7	82,1	0,7	2,8
29	0,40	0,7	26,6	66,6	0,7	5,3
31	0,49	0,5	16,1	80,4	0,4	2,6
33	0,19	1,0	55,4	39,1	1,2	3,3

Doebern, Mai 1998

Sedimenttiefe cm	Pges mg g ⁻¹	TP-NH ₄ Cl %	TP-BD %	TP-NaOH %	TP-HCL %	TP-Residual %
1	0,43	0,8	16,1	77,2	1,6	4,3
3	0,72	0,5	13,3	81,3	0,8	4,2
5	0,49	0,8	14,1	79,7	1,4	4,0
7	0,36	1,0	18,8	73,8	1,9	4,5
9	0,35	0,8	15,2	78,8	1,5	3,8
11	0,55	0,7	16,4	79,3	1,0	2,6
13	0,43	0,8	16,1	80,7	1,1	1,4
15	0,41	0,8	15,5	80,9	1,4	1,4
17	0,42	0,7	12,2	84,5	1,2	1,4
19	0,63	0,3	15,1	81,2	0,8	2,5
21	0,89	0,3	13,3	84,3	0,6	1,5
23	0,35	0,7	11,4	85,5	1,2	1,1
25	0,45	0,5	14,1	81,4	0,9	3,1
27	0,45	0,5	17,3	79,4	1,5	1,4
29	0,55	0,4	20,4	73,3	0,9	5,0
31	0,31	0,7	12,5	83,4	1,1	2,3
33	0,33	0,6	13,8	76,5	1,0	8,1

P-Extraktion**Experiment 1, 8 Wochen**

Sedimenttiefe	P _{ges}	TP-NH ₄ Cl	TP-BD	TP-NaOH	TP-HCl
cm	mg g ⁻¹	%	%	%	%
1	0,69	0,3	71,1	28,5	0,1
2	0,52	0,4	64,7	34,7	0,1
3	0,46	0,6	53,8	45,5	0,1
4	0,50	0,4	84,2	15,3	0,1
5	0,24	0,6	77,8	21,4	0,1
7	0,04	0,5	88,0	11,5	0,1
9	0,07	0,4	90,1	9,4	0,1
11	0,19	0,4	90,1	9,4	0,1
12	0,12	0,8	82,0	17,1	0,1
13	0,05	0,8	81,3	17,8	0,1
14	0,05	1,9	72,7	25,2	0,2
15	0,03	1,5	64,6	33,7	0,2

Experiment 2, 8 Wochen

Sedimenttiefe	P _{ges}	TP-NH ₄ Cl	TP-BD	TP-NaOH	TP-HCl
cm	mg g ⁻¹	%	%	%	%
1	77,60	0,1	23,4	76,1	0,4
2	74,47	0,0	38,2	61,4	0,4
4	5,38	0,1	53,1	46,7	0,1
5	2,12	0,2	59,4	40,0	0,3
7	0,30	2,7	49,0	46,8	1,4
9	0,21	0,9	47,2	49,7	2,1
11	0,27	1,2	90,8	6,4	1,6
13	0,12	3,1	90,2	5,4	1,2
15	0,05	5,6	77,6	14,1	2,7
17	0,08	2,3	52,2	35,3	10,3
19	0,11	4,0	53,1	36,1	6,8
21	0,09	1,9	59,0	32,0	7,1
23	0,04	4,1	68,3	16,3	11,2
25	0,04	3,0	68,2	25,0	3,9
27	0,05	3,5	81,1	9,5	5,9
29	0,11	1,1	74,4	22,8	1,8
31	0,03	2,0	66,5	19,6	11,9

Experiment 3, 8 Wochen

Sedimenttiefe	P _{ges}	TP-NH ₄ Cl	TP-BD	TP-NaOH	TP-HCl
cm	mg g ⁻¹	%	%	%	%
1	84,04	0,5	35,4	63,9	0,2
2	90,03	0,3	25,6	74,0	0,0
3	70,14	0,1	20,0	79,9	0,0
4	12,53	0,1	62,8	37,0	0,1
5	2,44	0,3	72,1	27,3	0,4
7	0,58	2,3	59,4	37,1	1,2
9	0,48	0,9	44,7	53,4	0,9
10	0,56	0,6	44,1	54,7	0,5

Die residualen P-Gehalte wurden vernachlässigt (keine Messungen vorhanden)
und die prozentuale Verteilung der restlichen Fraktionen auf 100 % bezogen

P-Extraktion

Experiment 1, 16 Wochen

Sedimenttiefe	Pges	TP-NH ₄ Cl	TP-BD	TP-NaOH	TP-HCL	TP-Residual
cm	mg g ⁻¹	%	%	%	%	%
3	0,54	0,2	4,5	48,3	45,2	1,8
4	0,47	0,4	12,2	84,2	1,2	2,1
5	0,45	0,5	10,7	83,8	2,4	2,6
7	0,28	0,6	27,0	64,8	2,0	5,8
9	0,24	0,9	45,1	50,4	0,6	3,5
11	0,23	1,5	46,2	43,0	1,6	8,6
13	0,33	1,1	72,6	25,4	0,5	1,2
15	0,44	1,2	53,2	39,7	1,4	5,2
17	0,19	0,9	36,8	53,3	2,5	6,9
19	0,17	1,1	44,0	44,7	2,3	8,6
21	0,19	0,0	89,7	0,0	1,5	8,5
23	0,16	1,8	58,7	27,4	3,9	9,5
25	0,15	2,3	55,5	23,6	7,5	12,9
27	0,11	3,7	54,7	23,1	5,8	15,6
29	0,23	4,7	73,0	14,6	4,5	7,3
31	0,18	4,6	67,7	17,6	3,8	10,1

Experiment 2, 16 Wochen

Sedimenttiefe	Pges	TP-NH ₄ Cl	TP-BD	TP-NaOH	TP-HCL	TP-Residual
cm	mg g ⁻¹	%	%	%	%	%
1	85,08	0,0	13,0	86,3	0,2	0,6
2	7,80	0,0	33,5	65,3	0,8	0,5
3	1,74	0,1	66,6	32,4	0,2	0,7
4	1,11	0,2	60,6	37,8	0,3	1,0
5	0,89	0,4	54,0	42,7	0,5	2,3
7	0,37	0,3	69,9	26,6	0,3	2,8
9	1,04	0,2	87,8	10,4	0,2	1,5
11	0,24	0,6	73,3	22,1	0,6	3,5
12	0,47	0,2	48,0	50,1	0,2	1,5
13	0,17	0,5	59,2	36,3	0,5	3,5
14	0,21	0,4	74,1	22,2	0,4	2,9

Experiment 3, 16 Wochen

Sedimenttiefe	Pges	TP-NH ₄ Cl	TP-BD	TP-NaOH	TP-HCL	TP-Residual
cm	mg g ⁻¹	%	%	%	%	%
1	93,23	0,2	11,7	86,8	0,8	0,4
2	55,90	0,0	28,8	70,1	0,7	0,3
3	17,71	0,0	49,6	49,6	0,6	0,2
4	6,05	0,0	34,6	64,3	0,6	0,5
5	3,75	0,1	33,0	65,3	1,1	0,6
7	0,66	0,2	85,0	13,1	0,3	1,4
9	1,63	0,2	73,3	25,1	0,6	0,8
11	1,16	0,2	30,8	67,6	0,2	1,2
13	0,59	0,3	51,0	46,9	0,3	1,4
15	0,66	0,4	39,1	57,8	0,5	2,2
17	0,32	0,4	61,0	36,0	0,4	2,3
19	0,17	1,0	54,9	37,4	1,0	5,6

P-Extraktion**Experiment 1, 24 Wochen**

Sedimenttiefe	P _{ges}	TP-NH ₄ Cl	TP-BD	TP-NaOH	TP-HCl	TP-Residual
cm	mg g ⁻¹	%	%	%	%	%
1	0,60	0,4	61,5	35,1	0,4	2,53
2	0,84	0,2	35,2	62,2	0,2	2,21
3	0,82	0,2	37,6	59,0	0,5	2,63
4	0,75	0,2	28,8	67,7	0,4	2,95
5	0,75	0,2	29,2	67,7	0,6	2,28
7	0,04	0,8	46,6	43,2	1,4	7,96
9	0,18	0,6	34,7	59,8	1,1	3,80
11	0,17	0,8	41,1	52,0	1,2	4,92
12	0,09	0,5	31,0	63,3	1,5	3,65
13	0,19	0,3	64,5	31,8	1,1	2,32
14	0,48	0,2	58,1	39,2	0,6	1,90
15	0,15	0,2	7,6	87,2	1,5	3,5

Experiment 2, 24 Wochen

Sedimenttiefe	P _{ges}	TP-NH ₄ Cl	TP-BD	TP-NaOH	TP-HCl	TP-Residual
cm	mg g ⁻¹	%	%	%	%	%
1	56,19	0,0	12,5	86,6	0,6	0,3
2	58,83	0,0	8,5	90,4	0,8	0,3
3	4,81	0,1	26,8	72,0	0,7	0,3
4	1,78	0,1	28,4	70,2	0,4	0,9
5	1,31	0,1	21,2	76,3	0,4	1,9
7	0,66	0,1	39,9	57,8	0,6	1,6
9	0,44	0,2	27,4	70,5	0,4	1,5
11	0,38	0,3	19,9	78,0	0,6	1,2
13	0,39	0,2	9,6	88,7	0,5	1,0
15	0,21	0,4	37,3	59,6	0,7	2,0
17	0,29	0,6	17,5	79,9	0,5	1,5
19	0,38	0,8	13,1	83,6	1,7	0,8
21	0,26	0,6	10,3	88,4	0,7	0,1

Experiment 3, 24 Wochen

Sedimenttiefe	P _{ges}	TP-NH ₄ Cl	TP-BD	TP-NaOH	TP-HCl	TP-Residual
cm	mg g ⁻¹	%	%	%	%	%
1	85,29	0,1	9,3	89,4	1,1	1,1
2	58,10	0,1	4,4	94,3	1,0	1,0
3	4,44	0,1	21,6	77,2	0,7	0,7
4	3,23	0,1	22,7	75,9	1,1	1,1
5	1,06	0,2	31,0	67,0	0,3	0,3
7	0,40	0,1	45,8	51,9	0,5	0,5
9	0,44	0,3	48,4	48,8	0,3	0,3
11	0,40	0,3	16,0	80,8	1,3	1,3
13	0,36	0,4	18,2	75,3	1,2	1,2
15	0,31	0,3	25,4	70,5	0,7	0,7
17	0,19	0,3	46,4	48,3	0,9	0,9
19	0,25	0,3	40,9	53,8	0,7	0,7
21	0,30	0,2	20,4	77,3	0,8	0,8
23	0,33	0,2	11,4	86,5	0,8	0,8
25	0,21	0,3	14,9	82,7	0,8	0,8
27	0,06	0,5	20,7	61,3	6,1	6,1

Fe-Extraktion

(Fe ascorbatlöslich/Fe dithionithlöslich)

Sedimenttiefe	Niemegk		Doebern	
	cm	Jul 97 Mai 98	Jul 97 Mai 98	
1	23,7	28,0	2,3	7,9
2	31,4	n.b.	n.b.	n.b.
3	23,9	41,8	1,4	1,5
4	22,8	n.b.	n.b.	n.b.
5	16,8	49,9	0,6	0,8
6	10,0	n.b.	n.b.	n.b.
7	3,3	54,2	0,7	0,9
8	5,7	n.b.	n.b.	n.b.
9	16,2	23,5	0,4	0,5
10	8,6	n.b.	n.b.	n.b.
11	7,9	16,5	0,3	0,4
13	14,2	6,8	0,5	0,4
15	9,8	3,3	0,4	0,3
17	3,9	2,3	0,3	0,4
19	6,0	0,8	0,4	0,3
21	n.b.	5,4	0,5	0,3
23	n.b.	5,0	0,4	0,3
25	n.b.	2,7	n.b.	0,2
27	n.b.	2,2	n.b.	0,2
29	n.b.	3,2	n.b.	0,3
31	n.b.	2,3	n.b.	0,2

S-Extraktion

(CRS-Chrom-Reduzierbarer Schwefel)

Sedimenttiefe	Niemegk	Sedimenttiefe	Experiment1		
	Mai 98		8 Wochen	16 Wochen	24 Wochen
cm	mg S/g DW	cm	mg S/g DW	mg S/g DW	mg S/g DW
0-2	0,26	0-1	0,37	n.b.	0,40
5-7	0,32	1-2	0,25	n.b.	0,47
10-12	0,54	2-3	n.b.	1,79	n.b.
14-16	0,22	6-7	0,36	n.b.	0,41
18-20	0,58	10-12	n.b.	12,23	n.b.
		12-13	n.b.	n.b.	0,33

Sedimenttiefe	Experiment2			Experiment 3		
	8 Wochen	16 Wochen	24 Wochen	8 Wochen	16 Wochen	24 Wochen
cm	mg S/g DW	mg S/g DW	mg S/g DW	mg S/g DW	mg S/g DW	mg S/g DW
0-1	0,79	2,76	11,37	0,72	2,62	10,28
1-2	0,37	0,61	10,18	1,22	1,05	2,04
3-4	n.b.	n.b.	0,76	n.b.	0,62	n.b.
6-7	0,28	n.b.	n.b.	0,62	n.b.	0,48
9-10	n.b.	0,37	n.b.	n.b.	n.b.	n.b.

Alle AVS-Gehalte der untersuchten Proben betrugen < 5% der CRS Gehalte.

Sedimentfallenmaterial**Niemegk, Mai 98**

Sedimentation g m ⁻² d ⁻¹	Pges mg g ⁻¹	TP-NH ₄ Cl %	TP-BD %	TP-NaOH %	TP-HCL %	TP-Residual %	Feasc/Fedith
21,95	0,85*	0,69*	94,30*	4,62*	0,39*	n.b.	39,7

* TP Residual wurde vernachlässigt (keine Messungen vorhanden), die restlichen P-Fractionen wurden auf 100% bezogen.

Niemegk, Nov 98

Sedimentation g m ⁻² d ⁻¹	Na mg g ⁻¹	Mg mg g ⁻¹	Al mg g ⁻¹	Si mg g ⁻¹	P μg g ⁻¹	K mg g ⁻¹	Ca mg g ⁻¹	Mn μg g ⁻¹	Fe mg g ⁻¹
28,10	0,93	2,61	65,07	135,66	666,72	10,49	2,36	92,00	173,63

Extraktionen	Pges mg g ⁻¹	TP-NH ₄ Cl %	TP-BD %	TP-NaOH %	TP-HCL %	TP-Residual %	Feasc/Fedith
	0,66	0	44,91	54,89	0	0,2	35,0

Algenmaterial

C mg g ⁻¹	Corg mg g ⁻¹ DW	N mg g ⁻¹ DW	S mg g ⁻¹ DW	P mg g ⁻¹ DW	Fe mg g ⁻¹ DW
347	336	64,4	6,08	5,79	3,02

